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VOL. III   SEPTEMBER 1934   PART II

CONTENTS

TRANSACTIONS

ON A THEOREM OF MERTENS ... ... S. M. SHAH 3

MAXIMUM MODULUS THEOREM ... ... D. D. KOSAMBI 11

ON A PROBLEM IN SERIES ... ... S. M. SHAH 13

ELLIPSOIDAL WAVE FUNCTIONS ... ... S. L. MALURKAR 16

THE TEMPERATURE-VARIATION OF THE VISCOSITIES OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES. G. R. PARANJPE & E. B. RAJDERKAR 21

SOME INTERPRETATIONS OF THE BAND SPECTROSCOPIC RESULTS OF NITROGEN ... ... N. R. TAWDE 53

A NEW METHOD OF COUNTING DUST NUCLEI IN AIR. G. R. PARANJPE & Y. G. NAIK 58

POLLUTION OF BOMBAY AIR BY SMOKE ... ... Y. G. NAIK 66

MOUNTING CONCAVE GRATINGS OF SMALL RADIUS OF CURVATURE ... ... H. N. DESAI 70

AN OPTICAL METHOD OF MEASURING POISSONS RATIO OF THIN GLASS PLATES ... ... V. D. MAJUMDAR 77

CONDENSATION OF PHENOLS AND PHENOLIC ETHERS WITH ACETONE-DICARBOXYLIC ACID, SYNTHESIS OF $\beta\beta$-SUBSTITUTED GLUTARIC ACIDS ... V. M. DIXIT & G. N GOKHALE 80

CONDENSATION OF PHENOLS WITH ACETONE-DICARBOXYLIC ACID, ANHYDRIDES OF β-2-HYDROXYPHENYL GLUTACONIC ACIDS ... ... V. M DIXIT & G. N. GOKHALE 95

STUDY OF THE ACTION OF SODIUM AND POTASSIUM ON COMPOUNDS CONTAINING THE—NH—GROUP ... S. V. SHAH & D. G. PISHAVIKAR 106

VISCOSITY OF MODERATELY AND HIGHLY CONCENTRATED SOLUTIONS OF SOME ELECTROLYTES IN WATER AND METHYL, ETHYL AND N-PROPYL ALCOHOLS AND A DISCUSSION OF RELATION BETWEEN CONDUCTANCE AND FLUIDITY ... ... H. N. DESAI, D. B. NAIK & B. N. DESAI 109

A STUDY OF THE CHEMICAL CHANGES DURING THE FORMATION AND GERMINATION OF THE RICE GRAIN. D. L. SAHASRABUDDHE & M. M. KIBE 121

CONDENSATION OF ACETONE-DICARBOXYLIC ACID WITH PHENOLS AND PHENOLIC ETHERS: PART II. FORMATION OF 3-KETO-4-METHYL-7-METHOXY HYDRINDENYLIDENE-ACETIC ACID ... ... D. B. LIMAYE & G. R. GOGATE 135

LIGHT FILTERS FOR THE MERCURY ARC ... B. K. VAIDYA 141

CHLORALIDES OF α-HYDROXY CARBOXYLIC ACIDS. (Late) A. N. MELDRUM & D. M. BHATT 149

ACTION OF BROMINE ON P-METHOXY SULPHONIC ACIDS. M. S. SHAH, C. T. BHATT AND D. D. KANGA 153

METHYLATION OF SOME SULPHO- AND NITRODERIVATIVES OF CRESOLS AND HYDROXY BENZOIC ACIDS. M. S. SHAH C. T. BHATT & D. D. KANGA 155

THE REACTION BETWEEN ACETYLENE AND SULPHUR. C. T. BHATT, K. S. NARGUND, D. D. KANGA & M. S. SHAH 159

CONDENSATION OF 4-BROMO-PHENOL AND BROMO-CRESOLS WITH BENZOIL CHLORIDE AND M-AND P-NITROBENZOYL CHLORIDES ... ... G. V. JADHAV & Y. I. RANGWALA 161

SYNTHETIC PRODUCTION OF CAMPHOR FROM PINENE. B. G. S. ACHARYA & T. S. WHEELER 163

SOME REACTIONS OF P-DIMETHYLAMINO-BENZO-PHENONE AND THE BECKMANN TRANSFORMATION OF P-DIMETHYL-AMINO-BENZO-PHENONE-OXIME R. C. SHAH & M. B. ICHAPORIA 172

ARTICLES

DEFINITION OF STEADY MOTION ... ... G. S. MAHAJANI 176

A NOTE ON REAL NUMBER, INFINITY AND CONTINUITY. D. P. PATRAVALI 180

ON THE FOCI OF CONICOIDS ... ... B. B. BAGI 186

PLANETARY CHART AND ASTRONOMICAL PHENOMENA FOR THE YEAR 1935 ... ... B. K. VAIDYA 188

IS MATHEMATICS AN ARTS OR A SCIENCE SUBJECT. N. M. SHAH 191

COLLOIDS IN THE ATMOSPHERE ... ... B. N. DESAI 195

SPATIAL CONFIGURATION OF CYCLOHEXANE AND ITS DERIVATIVES. ... ... R. D. DESAI 219

SUMMARIES AND ABSTRACTS OF THESES 226

OBITUARY 231

REVIEWS 237

ACKNOWLEDGMENTS 239

EXCHANGES 241

ON A THEOREM OF MERTENS

BY

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1. In the "elementary" theory of primes, there is a well-known result due to Mertens* that

$$\prod_{p\leqslant x}\left(1-\frac{1}{p}\right)\sim\frac{e^{-C}}{\log x}$$

C being Euler's constant.

$$\text{Let } P(x) = \prod_{p\leqslant x}\left(1-\frac{1}{p}\right)-\frac{e^{-C}}{\log x}$$

Assuming the known results in the theory of primes, *I prove here that*†

$$P(x)=O\left(e^{-\alpha\sqrt{\log x.\ \mathrm{ll}x}}\right) \qquad \text{. . . . . (1)}$$

and that

$$P(x)=O\left(1/\sqrt{x}\right) \text{ (On Riemann Hypothesis)} \qquad \text{. . . . (2)}$$

and

$$P(x)=\Omega\left(\frac{\mathrm{l}_3x}{\log^2 x}\frac{1}{\sqrt{x}}\right) \text{ (without any hypothesis)} \text{. . . .} \qquad (3)‡$$

---

*E, Landau, Handbuch, §36. A. E. Ingham, *The Distribution of Prime Numbers*, pp. 22-24. G. H. Hardy, "Note on a Theorem of Mertens," *Journal Lond. Math. Soc. II*, (1927), pp. 70-72 where other references are given.

†We write ll$x$ for loglog$x$ and l_3x for logloglog$x$.

‡The result (11) below—with the help of which we have proved (3) —is true whether we assume Riemann Hypothesis or not. In fact if R. H is false, then we have

$$\pi(x)-\int_2^x\frac{du}{\log u}=\Omega\left(x^{\Theta-\delta'}\right)$$

where Θ denotes the upper bound of the real part of the zeros of $\zeta(s)$, and δ' is any fixed positive number. With the help of this result we can prove—the proof is similar to that of (3)—, that

$$P(x)=\Omega\left(x^{\Theta-1-\delta}\right)=\Omega\left(\frac{1}{\sqrt{x}}\right)$$

if R. H is false; and this is obviously, a better result than (3).

LEMMA 1

$$\text{Let } R(x) = \sum_{p \leqslant x} \frac{1}{p} - \text{ll}x - B$$

$$\text{Then } R(x) = O\left(e^{-\frac{\alpha_1}{2}\sqrt{\log x.\, \text{ll}x.}}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$R(x) = O\,(\log x/\sqrt{x}) \text{ (On R. H)} \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\text{and } R(x) = \Omega\left(\frac{l_3 x}{\log x}\frac{1}{\sqrt{x}}\right) \text{ (without any hypothesis)} \; . \; . \; . \quad (6)$$

Proof.

$$\sum_{p \leqslant x} \frac{1}{p} = \sum_{n=2}^{[x]} \frac{\vartheta(n) - \vartheta(n-1)}{n \log n}$$

$$\text{where } \vartheta(x) = \sum_{p \leqslant x} \log p = x + \varepsilon(x) \quad \text{(say)}$$

$$\therefore \sum_{p \leqslant n} \frac{1}{p} = \sum_{n=2}^{[x]} \frac{1}{n \log n}$$

$$+ \sum_{2}^{[x]} \varepsilon(n) \left\{\frac{1}{n \log n} - \frac{1}{(n+1) \log (n+1)}\right\}$$

$$+ A_0 + \frac{\varepsilon([x])}{([x]+1) \log ([x]+1)}$$

$$= \text{ll}x + A_1 + O\left(\frac{1}{x \log x}\right) + \sum_{2}^{[x]} O\left(\frac{\varepsilon(n)}{n^2 \log n}\right)$$

$$+ O\left(\frac{\varepsilon(x)}{x \log x}\right) \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$\text{Now } \varepsilon(x) = \vartheta(x) - x = O\left(x e^{-\alpha_1 \sqrt{\log x.\, \text{ll}x}}\right) \; . \; . \; . \; . \; . \quad (8)^*$$

$$\therefore \sum_{2}^{[x]} O\left(\frac{\varepsilon(n)}{n^2 \log n}\right) = \sum_{2}^{[x]} O\left(\frac{1}{n \log n} \frac{1}{e^{\alpha_1 \sqrt{\log n.\, \text{ll}n}}}\right)$$

$$= D + O\left(\int_x^\infty \frac{du}{u \log u} \frac{1}{e^{\alpha_1 \sqrt{\log u.\, \text{ll}u}}}\right)$$

$$= D + O\left(e^{-\frac{\alpha_1}{2}\sqrt{\log x.\, \text{ll}\, x}} \int_x^\infty \frac{du}{u \log u} \frac{1}{e^{\frac{\alpha_1}{2}\sqrt{\log u.\, \text{ll}u}}}\right)$$

$$= D + O\left(e^{-\frac{\alpha_1}{2}\sqrt{\log x.\, \text{ll}x}}\right)$$

*Results (8) and (11) are due to Littlewood and (9) is due to Von Koch.

$$\therefore \sum_{p \leqslant x} \frac{1}{p} = \text{ll}x + B + O\left(e^{-\frac{\alpha_1}{2}\sqrt{\log x . \text{ll}x}}\right)$$

which proves (4).

On Riemann Hypothesis we have

$$I(x) = x + O\left(x^{\frac{1}{2}} \log^2 x\right) \quad \ldots \ldots \ldots \ldots \quad (9)^*$$

and hence $\sum_{2}^{x} O\left(\frac{\varepsilon(n)}{n^2 \log n}\right) = \sum_{2}^{x} O\left(\frac{\log n}{n^{3/2}}\right) = D_1 + O\left(\frac{\log x}{\sqrt{x}}\right)$

and hence from (7) we have†

$$R(x) = O\left(\frac{\log x}{\sqrt{x}}\right)$$

To prove (6), suppose if possible that

$$R(x) = o\left(\frac{l_3 x}{\log x} \frac{1}{\sqrt{x}}\right)$$

Then

$$\pi(x) = \sum_{p \leqslant x} 1 = \sum_{n=2}^{[x]} \left\{ S(n) - S(n-1) \right\} . n.$$

$$= S([x])([x]+1) - \sum_{2}^{[x]} S(n)$$

Where $S(n) = \sum_{p \leqslant n} \frac{1}{p}$

$$\therefore \sum_{2}^{[x]} S(n) = \sum_{2}^{[x]} \text{loglog}\, n + Bx + O(1) + \sum_{2}^{[x]} R(n)$$

$$= \int_{2}^{x} \text{loglog}\, u \, du + Bx + O(\text{loglog}\, x)$$

$$+ \sum_{2}^{[x]} o\left(\frac{l_3 n}{\log n} \frac{1}{\sqrt{n}}\right)$$

Now

$$\sum_{2}^{[n]} o\left(\frac{l_3 n}{\log n} \frac{1}{\sqrt{n}}\right) < O(1) + \varepsilon^1 \sum_{[n_0]+1}^{[x]} \frac{l_3 n}{\log n} \frac{1}{\sqrt{n}}$$

$$= O(1) + \varepsilon^1 O\left(\int_{n_0+1}^{x} \frac{l_3 u}{\log u} \frac{du}{\sqrt{u}}\right)$$

†We note that

$$B = \lim_{x=\infty} \left\{ \sum_{p \leqslant x} \frac{1}{p} - \text{loglog}\, x \right\}$$

$$= O(1) + \varepsilon^1 O\left(\int^{\sqrt{x}} \frac{l_3 y}{\log y} dy \right)$$

$$= o\left(\frac{\sqrt{x}}{\log x} l_3 x \right)$$

and $\int_2^x \log\log u \, du = x \, \mathrm{ll}x + O(1) - \int_2^x \frac{du}{\log u}$

$$\therefore \pi(x) = \int_2^x \frac{du}{\log u} + o\left(\frac{\sqrt{x}}{\log x} l_3 x\right) \quad \ldots\ldots\ldots (10)$$

But

$$\pi(x) = \int_2^x \frac{du}{\log u} + \Omega\left(\frac{\sqrt{x}}{\log x} . l_3 x\right) \quad \ldots\ldots\ldots (11)^*$$

Therefore we have a contradiction and therefore

$R(x) \neq o\left(\frac{l_3 x}{\log x} \frac{1}{\sqrt{x}}\right)$ which proves (6)

Now

$$\sum_{p \leqslant x} \log\left(1 - \frac{1}{p}\right) = -\sum_{p \leqslant x} \frac{1}{p} + \sum_{p \leqslant x} \left\{ \log\left(1 - \frac{1}{p}\right) + \frac{1}{p} \right\}$$

$$= -\sum_{p \leqslant x} \frac{1}{p} + \sum_{p} \left\{ \log\left(1 - \frac{1}{p}\right) + \frac{1}{p} \right\} + O\left(\sum_{n > x} \frac{1}{n^2}\right)$$

$$= -\mathrm{ll}x - B - R(x) + B - C + O\left(\frac{1}{x}\right)$$

$$\therefore \prod_{p \leqslant x}\left(1 - \frac{1}{p}\right) = \frac{e^{-C}}{\log x} \left\{ 1 - R(x) + o(R(x)) \right\}$$

$$\therefore P(x) = \prod_{p \leqslant x}\left(1 - \frac{1}{p}\right) - \frac{e^{-C}}{\log x}$$

$$= -\frac{e^{-C} R(x)}{\log x} + o\left(\frac{R(x)}{\log x}\right)$$

Hence from (4), (5) and (6), we have (1), (2) and (3) respectively.

It is interesting to compare the results

(I) $P(x) = o\left(\frac{1}{\log x}\right)$ ("Elementary")

(II) $P(x) = O\left(e^{-\alpha\sqrt{\log x . \mathrm{ll}x}}\right)$ ("Deep")

(III) $P(x) = O\left(1/\sqrt{x}\right)$ (On R. H.)

(IV) $P(x)=\Omega\left(\frac{l_3 x}{\log^2 x}\frac{1}{\sqrt{x}}\right)$ ("Deep", without any hypothesis)

(V) $P(x) = \Omega\left(\frac{1}{\sqrt{x}}\right)$ (If R. H is false)

2. *I prove here that, if* ν *be any fixed integer* $\geqslant 2$

$$\prod_{a\leqslant x}\left(1-\frac{1}{a}\right)=\exp.\left\{-\frac{(\mathrm{ll}x)^{\nu}}{\nu\,!}-\frac{B}{(\nu-1)\,!}(\mathrm{ll}x)^{\nu-1}+o\left((\mathrm{ll}x)^{\nu-1}\right)\right\} \quad (12)$$

where a *is a number having just* ν *prime factors*

$$\left(a=p_{\alpha_1}p_{\alpha_2}\ .\ .\ .\ p_{\alpha_\nu}\right)$$

$$\prod_{b\leqslant x}\left(1-\frac{1}{b}\right)=\exp.\left\{-\frac{(\mathrm{ll}x)^{\nu}}{\nu!}-\frac{B}{(\nu-1)!}(\mathrm{ll}x)^{\nu-1}+o\left((\mathrm{ll}x)^{\nu-1}\right)\right\} \quad (13)$$

where b *is a number, having* ν *prime factors, multiple prime factors being counted multiply.* $(a=p_{\alpha_1}^{\theta_1}\,p_{\alpha_2}^{\theta_2}\ .\ .\ .\ p_{\alpha_k}^{\theta_k}$ *where each* $\theta\geqslant 0$

and $\theta_1+\theta_2+.\ \ .\ \ .+\theta k=\nu$).

$$\prod_{c\leqslant x}\left(1-\frac{1}{c}\right)=\exp.\left\{-\frac{(\mathrm{ll}x)^{\nu}}{\nu!}+o\left((\mathrm{ll}x)^{\nu}\right)\right\}\ .\ .\ .\ .\ (14)$$

Where c *is a number having* ν *different prime factors,*

$\left(c=p_{\alpha_1}^{\theta_1}\ .\ .\ .\ p_{\alpha\nu}^{\theta_\nu}\right.$ *where each* $\theta>0\Big)$, *and* $\nu\geqslant 1$.

Since ν is supposed to be greater than unity, in (12) and (13), a constant is absorbed in the o term on the Right Hand side of (12) and (13). If $\nu = 1$ we have to take account of this constant.

LEMMA 2*.

$$\pi_{\nu}(x)=\sum_{a\leqslant x}1=\frac{x\,(\mathrm{ll}x)^{\nu-1}}{(\nu-1)\,!\log x}+\frac{Bx}{(\nu-2)!}\,\frac{(\mathrm{ll}x)^{\nu-2}}{\log x}$$

$$+o\left(\frac{x\,(\mathrm{ll}x)^{\nu-2}}{\log x}\right)\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ (15)$$

*Landau, Handbuch, §56. S. M. Shah, "On an Asymptotic Formulae for $\pi_n(x)$" to appear elsewhere. (15) and (16) are proved in this paper.

$$O_\nu(x) = \sum_{b \leqslant x} 1 = \frac{x\,(\mathrm{ll}x)^{\nu-1}}{(\nu-1)!\,\log x} + \frac{Bx}{(\nu-2)!}\,\frac{(\mathrm{ll}x)^{\nu-2}}{\log x}$$

$$+\, o\left(\frac{x\,(\mathrm{ll}x)^{\nu-2}}{\log x}\right) \quad \ldots\ldots\ldots\ldots (16)$$

$$\rho_\nu\,(x) = \sum_{c \leqslant x} 1 = \frac{x\,(\mathrm{ll}x)^{\nu-1}}{(\nu-1)!\,\log x} + o\left(\frac{x\,(\mathrm{ll}x)^{\nu-1}}{\log\ x}\right) \quad \ldots (17)$$

We prove (12). Proofs of (13) and (14) are similar.

$$\sum_{a \leqslant x} \log\left(1-\frac{1}{a}\right) = -\sum_{a \leqslant x}\frac{1}{a} + \sum_{a \leqslant x}\left\{\log\left(1-\frac{1}{a}\right) + \frac{1}{a}\right\}$$

$$= -\sum_{a \leqslant x}\frac{1}{a} + \sum_{a}\left\{\log\left(1-\frac{1}{a}\right) + \frac{1}{a}\right\} + O\left(\frac{1}{x}\right)$$

$$= -\sum_{a \leqslant x}\frac{1}{a} + K(\nu) + O\left(\frac{1}{x}\right)$$

where

$$K\,(\nu) = \sum_{a}\left\{\log\left(1-\frac{1}{a}\right) + \frac{1}{a}\right\}$$

Now

$$\sum_{a \leqslant x}\frac{1}{a} = \sum_{n=2}^{[x]} \frac{\pi_\nu(n) - \pi_\nu\,(n-1)}{n}$$

$$= \sum_{n=2}^{[x]} \frac{\pi_\nu(n)}{n(n+1)} + \frac{\pi_\nu([x])}{([x]+1)}$$

Now

$$\sum_{n=2}^{[x]} \frac{\pi_\nu(n)}{n(n+1)} = O\,(1) + \frac{1}{(\nu-1)!}\sum_{[n_1]+1}^{[x]} \frac{n\,(\mathrm{ll}n)^{\nu-1}}{\log n}\,\frac{1}{n(n+1)}$$

$$+ \frac{B}{(\nu-2)!}\sum_{[n_1]+1}^{[x]} \frac{n\,(\mathrm{ll}n)^{\nu-2}}{\log n}\,\frac{1}{n\,(n+1)}$$

$$+ \sum_{[n_1]+1}^{[x]} \theta\,\frac{n\,(\mathrm{ll}n)^{\nu-2}}{\log n}\,\frac{1}{n(n+1)}$$

where

$$|\,\theta\,| = |\,\theta\,(n)\,| < \varepsilon_1 \text{ if } n > n_1 = n_1\,(\varepsilon_1)$$

Further

$$\sum_{[n_1]+1}^{[x]} \frac{(\mathrm{ll}n)^{\nu-1}}{\log n}\,\frac{1}{n+1} = \int_{n_1+1}^{x} \frac{(\mathrm{ll}u)^{\nu-1}}{\log u}\,\frac{du}{u+1} + O\,(1)$$

$$= \int_{n_1+1}^{x} \frac{(\mathrm{ll}u)^{\nu-1}}{\log u} \frac{du}{u} + O(1)$$

$$= \frac{(\mathrm{ll}x)^{\nu}}{\nu} + O(1).$$

$$\sum_{n=2}^{[x]} \frac{\pi_\nu(n)}{n(n+1)} = \frac{(\mathrm{ll}x)^{\nu}}{\nu!} + \frac{B}{(\nu-1)!}(\mathrm{ll}x)^{\nu-1} + o\left((\mathrm{ll}x)^{\nu-1}\right) + O(1)$$

$$= \frac{(\mathrm{ll}x)^{\nu}}{\nu!} + \frac{B}{(\nu-1)!}(\mathrm{ll}x)^{\nu-1} + o\left((\mathrm{ll}x)^{\nu-1}\right)$$

Since $\nu > 1$.

$$\therefore \sum_{a \leqslant x} \frac{1}{a} = \frac{(\mathrm{ll}x)^{\nu}}{\nu!} + \frac{B}{(\nu-1)}(\mathrm{ll}x)^{\nu-1} + o\left((\mathrm{ll}x)^{\nu-1}\right)$$

$$\therefore \sum_{a \leqslant x} \log\left(1-\frac{1}{a}\right) = -\frac{(\mathrm{ll}x)^{\nu}}{\nu!} - \frac{B}{(\nu-1)!}(\mathrm{ll}x)^{\nu-1} + o\left((\mathrm{ll}x)^{\nu-1}\right)$$

which gives (12).

If $\nu = 1$ we use $\pi(x) = \pi_1(x) = \frac{x}{\log x} + o\left(\frac{x}{\log x}\right)$ instead of (12)

and get,

$$\sum_{p \leqslant x} \frac{1}{p} = \sum_{a \leqslant x} \frac{1}{a} = \mathrm{ll}x + B + o(1)$$

$$\therefore \sum_{p \leqslant x} \log\left(1-\frac{1}{p}\right) = -\mathrm{ll}x - B + K(1) + o(1)$$

$$= -\mathrm{ll}x - C + o(1)$$

which gives Mertens' result

$$P(x) = o\left(\frac{1}{\log x.}\right).$$

Finally we mention without proof a generalization of (1) in another direction.

$$\prod_{\substack{p \equiv l (\mathrm{mod}\ k) \\ p \leqslant x}} \left(1-\frac{1}{p}\right) = \frac{e^{-\beta}}{e^{\frac{1}{h}} . \mathrm{ll}x} \left\{ 1 + O\left(e^{-\alpha_2 \sqrt{\log x . \mathrm{ll}x}}\right) \right\}$$

B

where $h = \phi(k)$

$\beta = \beta\ (h, l)$ *a constant depending on h and l and* α_3 *is as an absolute positive constant.* We prove the above with the help of

$$\vartheta\ (x;\ k, l) = \sum_{\substack{p \equiv l\ (mod\ k) \\ p \leqslant x}} \log p = \frac{x}{h} + O\left(xe^{-\alpha_3 \sqrt{\log x\ llx}}\right)$$

If $k = 1$ $l = 1$ then $h = \phi\ (1) = 1$, $\beta\ (1, 1) = C$ and hence we get (1).

Similar generalizations of (2) and (3) can be proved with the help of the corresponding results for $\vartheta\ (x\ ;\ k, l)$.

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THE MAXIMUM MODULUS THEOREM

BY

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A fundamental result in the theory of functions of a complex variable is represented by the theorem :

If $f(z)$ be analytic in a closed region R, then max $|f(z)|$ is assumed on the boundary of R.

As corollaries, by considering $1/f(z)$, we see that $|f(z)|$ cannot have a non-zero minimum in the interior of R ; an application of the theorem to *exp* $f(z)$ shows that no harmonic function can have a maximum or a minimum within its region of definition.

The reach and bearing of the theorem has perhaps disguised the fact that it can easily be extended to non-analytic functions, *i.e.*, to transformations of the plane which are one to one and continuous, but need not be conformal. For instance, we may state a more general form :

THEOREM 1.

Hypothesis: $u(x,y)$, $v(x,y)$ are real functions of the real variables x,y, with continuous first partial derivatives and a non-vanishing Jacobian $J = \partial(u,v)/\partial(x,y)$ in some closed region R.

Conclusion: u^2+v^2 must assume its maximum value on the boundary and not within the interior of R.

Proof : There *is* a maximum value of $u^2 + v^2$, which, by the hypothesis, is a continuous function of the two variables in a closed region. This value cannot be taken on at an isolated interior point, for then, at that point, we should have

$$\frac{\partial}{\partial x}(u^2+v^2) \equiv 2u\frac{\partial u}{\partial x} + 2v\frac{\partial v}{\partial y} = 0$$

$$\frac{\partial}{\partial y}(u^2+v^2) \equiv 2u\frac{\partial u}{\partial y} + 2v\frac{\partial v}{\partial y} = 0$$

This gives $J=0$, contradictory to the assumption, or $u=v=0$ at the point. But the latter cannot represent a maximum value unless u, v, are identically null, which would again give $J=0$.

If the maximum be assumed along a curve (or for that matter a dense set of points), say the curve C, then $|\partial(u^2+v^2)/\partial s|_c=0$, and as the value is a maximum, we should also have the directional derivative along any curve cutting C vanish at the point of intersection.

But if these two derivatives vanish, then it is clear that the partial derivatives with respect to x,y, vanish all along the curve, which leads to the same contradiction as above. Therefore, the maximum is not only assumed on the boundary, but actually greater than any interior value.

Q. E. D.

The same reasoning shows that u^2+v^2 cannot have a non-zero minimum in the interior of R. Furthermore, neither u nor v can have a maximum or a minimum within R. A general theorem covers all of these cases :

THEOREM 2.

Under the assumptions of theorem 1, no function $\varphi(u,v)$ with continuous first partial derivatives can have a maximum or a minimum at an interior point of R unless $\partial\varphi/\partial u = \partial\varphi/\partial v = 0$ at that point.

The proof is as indicated before.

Whereas the transformations considered are not conformal, and hence, do not correspond to the more restricted class of functions satisfying the Cauchy-Riemann differential equations, it is clear nevertheless that they are not so general as might be wished, being in fact *schlicht* in R, due to the non-vanishing Jacobian. For the general case, exception would have to be made of points where the inverse transformation failed because of the vanishing of J.

ON A PROBLEM IN SERIES

BY

S. M. SHAH

There is a misprint in problem 137, p. 312, of Knopp Infinite Series*. The problem is stated as follows :

If Σd_n is a divergent series, with $d_n \to 0$ (d_n's are all positive) and if the D_n's are its partial sums we have

$$\sum_{\nu=1}^{n} d_\nu D_\nu \sim \tfrac{1}{2} D_n \qquad \ldots \ldots \ldots \ldots \ldots (1)$$

If we take for example, $d_n = 1/n$, then $D_n \sim \log n$ and

$$\sum_{\nu=1}^{n} d_\nu D_\nu \sim \sum_{\nu=1}^{n} \frac{\log \nu}{\nu} \sim \tfrac{1}{2} (\log n)^2$$

The example suggests that R. H. S. of (1) is $\frac{1}{2} D_n^2$.

I first prove a general theorem.

Th. I.

If (1) $d_n \geqslant 0$

(2) Σd_n is a divergent series and D_n's are its partial sums.

(3) $d_n / D_{n-1} \to a$ $(0 \leqslant a \leqslant \infty)$.

then it follows that

$$\sum_{\nu=1}^{n} d_\nu D_\nu \sim \frac{a+1}{a+2} D_n^2$$

Proof.

$$\text{From (3) we get} \quad \frac{d_n D_n}{D_n^2 - D_{n-1}^2} \to \frac{a+1}{a+2}$$

$$\therefore -\varepsilon\, (D_n^2 - D^2_{n-1} < d_n D_n - (D^2_{n-1} - D^2_{n-1}) \frac{a+1}{a+2} < \varepsilon\, (D_n^2 - D^2_{n-1})$$

for every $n > n_0 = n_0(\varepsilon)$

Taking the R.H.S. inequality and adding all such inequalities for $n = n_0+1, n_0+2, .., N$.

$$\sum_{n_0+1}^{N} d_n D_n < \left(\frac{a+1}{a+2}\right) (D_N^2 - D_{n_0}^2) + \varepsilon\, (D_N^2 - D_{n_0}^2)$$

*There is no misprint in the second German edition of the book.

$$\therefore \quad \sum_{1}^{N} d_n D_n < K + \left(\frac{a+1}{a+2} + \varepsilon\right) (D_N^2 - D_{n_0}^2)$$

where K is a constant.

$$\therefore \quad \overline{\lim_{N=\infty}} \; \frac{1}{D_N^2} \sum_{n=1}^{N} d_n D_n \leqslant \frac{a+1}{a+2}$$

$$\text{Similarly} \; \underline{\lim_{N=\infty}} \; \frac{1}{D_N^2} \sum_{n=1}^{N} d_n D_n \geqslant \frac{a+1}{a+2}$$

and these two inequalities give the required result.

COR.

Let $a = 0$ we get

If Σd_n is a divergent series of positive terms, $d_n = o(D_n)$.

$$\text{then} \quad \sum_{\nu=1}^{n} d_\nu D_\nu \sim \tfrac{1}{2} D_n^2.$$

This proves the problem mentioned in the beginning.

TH. II

If Σd_n is a divergent series of positive terms and

$$\text{if} \quad \sum_{\nu=1}^{n} d_\nu D_\nu \sim \tfrac{1}{2} D_n^2,$$

then $d_n = o\ (D_n)$.

REMARK.

We note that if $\sum_{\nu=1}^{n} d_\nu D_\nu \sim l D_n^2$ then $\frac{1}{2} \leqslant l \leqslant 1$. For suppose l to be otherwise. By a well-known th.

$$\underline{\lim} \; \frac{d_n D_n}{D_n^2 - D^2_{n-1}} \leqslant \underline{\lim} \; \frac{\sum_{\nu=1}^{n} d_\nu D_\nu}{D_n^2} \leqslant \overline{\lim} \; \frac{d_n D_n}{D_n^2 - D^2_{n-1}}$$

$$\therefore \underline{\lim} \; \frac{D_n}{D^n + D_{n-1}} \leqslant l \leqslant \overline{\lim} \; \frac{D_n}{D_n + D_{n-1}}$$

If now $l = \frac{1}{2} - k$ where $k > 0$

$$\text{Then} \; \underline{\lim} \; \frac{D_n}{D_n + D_{n-1}} \leqslant \tfrac{1}{2} - k.$$

But since $D_{n-1} \leqslant D_n$.

$$\therefore \; \underline{\lim} \; \frac{D_n}{D_n + D_{n-1}} \geqslant \tfrac{1}{2}.$$

$\therefore$ Contradiction and hence $l \geqslant \frac{1}{2}$. Now suppose $l = 1+\theta$ where $\theta > 0$ then $1+\theta \leqslant \overline{\lim} \dfrac{D_n}{D_n + D_{n-1}}$ which is impossible.

Hence $\frac{1}{2} \leqslant l \leqslant 1$.

Proof

We have for $n > n_0 = n_0(\varepsilon)$

$$(\tfrac{1}{2}-\varepsilon) D_n^2 < \sum_{1}^{n} d_\nu D_\nu < (\tfrac{1}{2}+\varepsilon) D_n^2$$

and if $n-1 > n_0$, then

$$(\tfrac{1}{2}-\varepsilon) D^2_{n-1} < \sum_{\nu-1}^{n-1} d_\nu D_\nu < (\tfrac{1}{2}+\varepsilon) D^2_{n-1}$$

From these two inequalities we get

$$-2\varepsilon < \frac{d_n D_n - \frac{1}{2}(D_n^2 - D^2_{n-1})}{D_n^2} < 2\varepsilon$$

$$\therefore \lim_{n\to\infty} \frac{d_n^2}{D_n^2} = 0$$

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ELLIPSOIDAL WAVEFUNCTIONS

BY

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In a forthcoming issue of the *Indian Journal of Physics* a memoir on Ellipsoidal Wavefunctions is appearing. A few of the main results are brought together here.

In applied mathematics the D'alembertian equation

$$\partial^2\phi/\partial x^2 + \partial^2\phi/\partial y^2 + \partial^2\phi/\partial z^2 = \partial^2\phi/c^2\partial t^2$$

is of frequent occurrence. The solutions which could readily be applied to different boundary problems have attracted many workers. The above memoir deals with normal functions with a view to apply to boundaries consisting of ellipsoids or other central quadrics.

The system of confocal quadrics is taken as

$$x^2/(\lambda - e_3) + y^2/(\lambda - e_2) + z^2/(\lambda - e_1) = 1$$

where e_1, e_2, e_3 are real and $e_1 > e_2 > e_3$ and $e_1 + e_2 + e_3 = 0$. The ellipsoidal co-ordinates are $\lambda\ \mu\ \nu$. Denoting for shortness

$$\Delta^2_\lambda = (\lambda - e_1)(\lambda - e_2)(\lambda - e_3)$$

and similar symbols for μ and ν, and assuming that ϕ is proportional to $exp\ (ipt)$ the wave equation reduces to separable equation given by

$$\sum_\lambda \Delta_\lambda (\mu - \nu) \frac{\partial}{\partial\lambda}\left(\Delta_\lambda\, \partial\phi/\partial\lambda\right)$$
$$- (\lambda - \mu)(\mu - \nu)(\nu - \lambda)\, p^2\phi/4c^2 = 0.$$

If the solution is assumed to be of form $\Lambda(\lambda)\, M(\mu)\, N(\nu)$ the three functions $\Lambda(\lambda)$, $M(\mu)$ and $N(\nu)$ satisfy the same differential equation, *viz.*,

$$(\lambda - e_1)(\lambda - e_2)(\lambda - e_3)\left[d^2\Lambda/d\lambda^2 + \tfrac{1}{2}.\left\{1/(\lambda - e_1) + 1/(\lambda - e_2)\right.\right.$$
$$\left.\left. + 1/(\lambda - e_3)\right\} d\Lambda/d\lambda\right] - (a_0 + a_1\lambda - p^2\lambda^2/4c^2)\,\Lambda = 0$$

where a_1 and a_0 are arbitrary constants whose values have to be restricted by conditions similar to those imposed in the case of Mathieu functions. The condition is that ϕ is one valued, bounded and has bounded derivatives in the finite region of $x\ y\ z$.

The equation has singularities with exponents 0 and $\frac{1}{2}$ at e_1, e_2 and e_3 and an irregular singularity at infinity, and is a confluent form of differential equation with six regular singularities.

As the differential equations are more tractable when the variables are uniformised, new variables are chosen so that $\wp(\alpha) = \lambda$; $\wp(\beta) = \mu$; $\wp(\gamma) = \nu$ and $\wp(\omega_r) = e_r$ $(r = 1, 2 \text{ or } 3)$ and giving rise to the transformed equation

$$\sum_{\alpha\beta\gamma} [\wp(\beta)-\wp(\gamma)]\, \partial^2\phi / \partial\alpha^2$$

$$-\ [\wp(\beta)-\wp(\gamma)]\ [\wp(\gamma)-\wp(\alpha)]\ [\wp(\alpha)-\wp(\beta)]\ p^2\phi/c^2 = 0.$$

The Jacobean form of the equation is obtained by taking

$$x = q/k'.\quad dn\,\xi\ dn\,\eta\ dn\,\zeta.$$
$$y = -iqk^2/k'.\quad cn\,\xi\ cn\,\eta\ cn\,\zeta.$$
$$z = -iqk^2.\quad sn\,\xi\ sn\,\eta\ sn\,\zeta.$$

where

$$q = \underset{+}{\sqrt{}}(e_1-e_3)$$

and

$$k^2 = (e_1-e_2)\ /\ (e_1-e_3)$$
$$k'^2 = (e_2-e_3)\ /\ (e_1-e_3)$$

is

$$\sum_{\xi\eta\zeta} (sn^2\eta - sn^2\zeta)\ \partial^2\phi/\partial\zeta^2$$

$$+\ (sn^2\xi - sn^2\eta)\ (sn^2\eta - sn^2\zeta)\ (sn^2\zeta - sn^2\xi).\ n^2k^4\phi = 0.$$

where $n = pq/c$. The corresponding single variable equation is

$$d^2\,U/d\xi^2 + (a_0 - a_1 k^2 sn^2\,\xi - n^2k^4 sn^4\,\xi)\,U = 0.$$

The restrictive conditions are that U is a doubly periodic function of ξ and has bounded derivatives at all points except at points congruent to $\xi = iK'$ or $2K + iK'$.

The Jacobean form of the equation is simple for working.

The solution of the differential equation with the above condition is of form

$$(sn\xi)^{\sigma_1}\,(cn\xi)^{\sigma_2}\,(dn\xi)^{\sigma_3}\,\psi\,(sn^2\xi)\,;\ \sigma_1, \sigma_2, \sigma_3 = 0 \text{ or } 1$$

and where ψ is an integral function of $sn\xi$. It is shown also that $V(\xi)$ the second solution of the differential equation has different symmetry properties from the first. The characteristic functions may be taken to be the bounded solutions corresponding to those arbitrary

constants for which a solution with the above restrictive conditions is possible.

Two orthogonal relations are satisfied by the characteristic functions. Writing $U(\xi \mid a_1 a_0)$ to indicate definitely the constants involved we have

$$\int U(\xi \mid a_1\, a_0)\ U(\xi \mid a_1\, a'_0)\ d\xi = 0 \qquad a_0 \neq a'_0$$

$$\int\int U(\xi \mid a_1\, a_0)\, U(\eta \mid a_1\, a_0)\, U(\xi \mid a'_1\, a'_0)\, U(\eta \mid a'_1 a'_0)$$
$$\times\ (sn^2\xi - sn^2\eta)\ d\xi\ d\eta = 0$$

if $a_1 \neq a'_1$ and $a_0 \neq a'_0$ *or* if $a_1 = a'_1$ and $a_0 \neq a'_0$.
where the limits of integration are given by :

$$-\ 2\,K < \xi < 2\,K, \qquad \eta \text{ from } K - 2i\,K' \text{ to } k + 2i\,K'.$$

From the orthogonal relations it follows that the characteristic constants are real and that the characteristic functions are linearly independent.

From the general solution which is bounded at the origin of

$$\partial^2\phi / \partial x^2 + \partial^2\phi / \partial y^2 + \partial^2\phi / \partial z^2 = \partial^2\phi / c^2\partial t^2$$

in the form

$$\int\int F\left(1/k' \cdot x\,dn\,u\,dn\,v + i\,k/k' \cdot y\,cn\,u\,cn\,v + kz\,sn\,u\,sn\,v + ct\,;\ u;\ v\right)$$
$$\times\ du\,dv \quad . \quad . \quad . \quad .$$

ranges $-2\,K < u < 2\,K$; $\quad v$ from $K - 2i\,K'$ to $K + 2i\,K'$.
it is deduced that

$$U(\xi) = \text{const} \int\int U(\eta)\, U(\zeta)(sn^2\eta - sn^2\zeta)\, f(\xi\eta\zeta)\ d\eta\ d\zeta$$

ranges $-\ 2\,K < \eta < 2\,K$ and ζ from $K - 2i\,K'$ to $K + 2i\,K'$
where the nucleus $f(\xi\eta\zeta)$ is a symmetrical (in the variables) bounded and continuously differentiable solution of

$$\sum_{\xi\eta\zeta} (sn^2\eta - sn^2\zeta)\, \partial^2 f / \partial\xi^2$$
$$+\ n^2k^4\,(sn^2\xi - sn^2\eta)\,(sn^2\eta - sn^2\zeta)\,(sn^2\zeta - sn^2\xi)\,f = 0.$$

the same equation in the Jacobean form with which we started.

A similar result is found when the Weirstrassian elliptic functions are used.

The integral equations are nonlinear and hence the convention is made that the solutions are always used in the normal form. Under these conditions it is found that the solutions for the integral equations can be determined and it is observed that the constant has only discrete values.

The actual nuclei for the eight types and four species are given here. As the functions consist of two factors, one being

$$(sn\xi)^{\sigma_1}\ (cn\xi)^{\sigma_2}\ (dn\xi)^{\sigma_3}$$

and the other an integral function of $sn\xi$, a tabular arrangement of the first factor is given.

$$1. \qquad \begin{matrix} sn\,\xi, & cn\,\xi\ sn\,\xi & \\ cn\,\xi, & dn\xi\ cn\,\xi, & sn\,\xi\ cn\,\xi\ dn\,\xi, \\ dn\,\xi, & sn\,\xi\, dn\,\xi, & \end{matrix}$$

The corresponding integral equations are :—

Factor. 1,

$$U(\xi) = ic \int\int \cosh(nk^2\, sn\xi\, sn\eta\, sn\zeta)\,(sn^2\eta - sn^2\zeta)\, U(\eta)\, U(\zeta)\, d\eta d\zeta.$$

Factor. $sn\xi$,

$$U(\xi) = ic \int\int \sinh(nk^2 sn\xi\, sn\eta\, sn\zeta)\,(sn^2\eta - sn^2\zeta)\, U(\eta)\, U(\zeta)\, d\eta d\zeta.$$

Factor. $cn\xi$,

$$U(\xi) = -ic \int\int \sinh(nk^2/k'.\ cn\xi\, cn\eta\, cn\zeta)\,(sn^2\eta - sn^2\zeta)\, U(\eta)\, U(\zeta)\, d\eta\, d\zeta$$

Factor. $dn\xi$,

$$U(\xi) = ic \int\int \sin(n/k'.\, dn\xi\, dn\eta\, dn\zeta)\,(sn^2\eta - sn^2\zeta)\, U(\eta)\, U(\zeta)\, d\eta d\zeta.$$

Factor. $sn\xi\ cn\xi$,

$$U(\xi) = -ic \int\int cn\xi\, cn\eta\, cn\zeta\, \sinh(nk^2\, sn\xi\, sn\eta\, sn\zeta)\,(sn^2\eta - sn^2\zeta).\ U(\eta)\, U(\zeta)\, d\eta\, d\zeta.$$

Factor. $cn\xi\ dn\xi$,

$$U(\xi) = -ic \int\int dn\xi\, dn\eta\, dn\zeta\, \sinh(nk^2/k'.\ cn\xi\, cn\eta\, cn\zeta)\,(sn^2\eta - sn^2\zeta)\, U(\eta)\, U(\zeta)\, d\eta d\zeta.$$

Factor. $dn\xi\ sn\xi$,

$$U(\xi) = ic \int\int sn\xi\, sn\eta\, sn\zeta\, \sin(n/k'.\ dn\xi\, dn\eta\, dn\zeta)\,(sn^2\eta - sn^2\zeta)\, U(\eta)\, U(\zeta)\, d\eta d\zeta.$$

Factor. $sn\xi\ cn\xi\ dn\xi$,

$$U(\xi) = -ic \int\int sn\xi\, sn\eta\cdot sn\zeta\, cn\xi\, cn\eta\, cn\zeta\, \sin(n/k'.\ dn\,\xi\, dn\eta\, dn\zeta)\times (sn^2\eta - sn^2\zeta)\, U(\eta)\, U(\zeta)\, d\eta d\zeta.$$

In addition every characteristic function satisfies the normalising condition that

$$i\int\int (sn^2\eta - sn^2\zeta)\Big[U(\eta)\, U(\zeta)\Big]^2 d\eta d\zeta = \pm 1$$

according as the characteristic function has not or has a factor of type $cn\xi$. The limits are the same for all the integrals, *i.e.*

$$-2\,K < \eta < 2\,K' \text{ and } v \text{ from}$$
$$K-2iK' \text{ to } K+2iK'.$$

From the integral equations it is possible to deduce approximations to the characteristic functions when n is small. When $|\,sn\xi\,|$ is large, and n moderate by the application of the method of stationary phase the asymptotic expressions for the characteristic functions can be obtained. It follows simply from the asymptotic expressions for large and positive values of $sn\xi$ that the second solution of the differential equation is not a characteristic function.

Starting from the differential equation it is possible to deduce asymptotic expressions for the characterictic functions for large values of n. The actual work involved is also less than for the other expressions.

In $d^2\,U(\xi)/d\,\xi^2-(n^2\,k^4\,sn^4\,\xi+a_1\,k^2sn^2\,\xi-a_0)\,U(\xi)=0.$
it is assumed that

$$U=exp\ (nX)\ Y\left\{1+f_1/n+\ f_2/n^2+\ .\ \ .\ \ ,\right\}$$

where X, Y, f_1, f_2, etc., are functions of ξ only. It is also assumed that

$$a_1=\alpha_{-2}\,n^2+\alpha_{-1}\,n+\alpha_0+\alpha_1/n+\alpha_2/n^2\quad .\ .\ .$$
$$a_0=\beta_{-2}\,n^2+\beta_{-1}n+\beta_0+\beta_1/n+\beta_2/n^2\quad .\ .\ .$$

Substituting in the differential equation and comparing the coefficients of n and taking account of the fact that the resulting solutions are doubly periodic and assuming that f_1, f_2, etc., have no constant term, it is possible to deduce the values for $U(\xi)$. When n is real the expression has the form

$$\frac{exp\ (\pm nk\ sn\ \xi)}{\sqrt{cn\ \xi\ dn\xi}}\left(\frac{1+sn\ \xi}{cn\ \xi}\right)^{\pm\,(l+\frac{1}{2})}\left(\frac{1+\ ksn\ \xi}{dn\ \xi}\right)^{\mp(m+\frac{1}{2})}$$

neglecting terms of order $O(1/n)$, where l and m are integers.

The characteristic function is

$$U\ (\xi)\sim A\Big[\,exp\ (nk\ sn\ \xi)\ Y_1\pm\ exp\ (-nk\ sn\ \xi\,)\ Y_2\Big]$$

where Y_1 and Y_2 are equal to

$$\frac{1}{\sqrt{cn\ \xi\ dn\ \xi}}\left(\frac{1+sn\ \xi}{cn\ \xi}\right)^{(l+\frac{1}{2})}\left(\frac{1+k\ sn\xi}{dn\ \xi}\right)^{-(m+\frac{1}{2})}$$

$$\text{and}\quad\frac{1}{\sqrt{cn\ \xi\ dn\ \xi}}\left(\frac{1+sn\ \xi}{cn\ \xi}\right)^{-(l+\frac{1}{2})}\left(\frac{1+k\ sn\ \xi}{dn\ \xi}\right)^{(m+\frac{1}{2})}$$

THE TEMPERATURE-VARIATION OF THE VISCOSITIES OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES

BY

G. R. PARANJPE AND E. B. RAJDERKAR

(A)

NATURE OF THE PRESENT WORK

Introductory.

While a considerable amount of work has appeared on the viscosity of pure liquids and its variation with temperature, comparatively little has been done on the viscosity of solutions and its variation with regard to concentration and temperature. Solutions of non-electrolytes have been worked upon, but, as Hatschek points out (Viscosity of Liquids, Bell and Sons ; p. 131, 1928), "the variation of viscosity with temperature in solutions of electrolytes has not received much attention".

Herz and Martin (Zeit, anorg. Chem., *132*, 41 ; 1924) have tried to represent the fluidity of solutions of NaCl, Na_2SO_4, K_2SO_4, KI, and oxalic acid between temperatures 20° and 90° by Batschinski's formula (Z. phys. Chem., *84*, 613 ; 1931).

$$1/\eta = \phi = (v-w)/c$$

where v is specific volume, w and c constants, and by a linear formula proposed by Meyer and Rosencranz (Wied. Ann., *2*, 387 ; 1877).

$$\phi = a + b\mathrm{T}$$

where, again, a and b are constants and T is the absolute temperature. But the agreement between the value of the coefficient of viscosity obtained experimentally and that calculated is far from satisfactory, as, except in two or three cases, the error is as high as 7 to 8 per cent. With electrolytic solutions, other formulæ connecting viscosity and temperature, fail to give a fair agreement with experimental results.

Also the attempts, by various investigators, to correlate viscosity and concentration of an electrolytic solution, are, as is well known, mostly inadequate. Thus the equations of Einstein (Ann. Phys., *19*, 289 ; 1906), of Herz (Z. anorg. Chem., *99*, 132 ; 1917) and of Finkelstein (Phys. Z., *31*, 130 ; 1930) do not admit of the possibility of "negative viscosity" ; that of Arrhenius (Z. Phys. Chem. *1*, 285, 1887), predicts no minimum in either relative viscosity or viscosity

increment; that of Applebey (J. Chem. Soc. *97*, 2002, 1910) predicts a viscosity increment minimum but gives wrong hydration numbers, as in the case of $RbNO_3$ and other salts; the semi-empirical equation of Grüneisen (Wiss. Abh. P. T. R. *4*, 151, 237, 1905), in spite of its three arbitrarily fixed constants, is equally unsatisfactory. The equation of Jones and Dole (J. Am. Chem. Soc., *51*, 2950; 1929), which adequately represents viscosity concentration curves at low concentrations, is valid upto a limit of dilute concentration.

A systematic study of the change of viscosity with temperature and concentration, therefore, appears to be of some interest.

The present work.

The present work was undertaken with a view to study how the viscosity of strong electrolytes in solution with water varies with temperature at normal concentrations.

On the assumption that a common ion would facilitate comparison, the electrolytes chosen were all chlorides and had a common anion. The solvent was water in all cases. Another reason, why these salts were chosen, is that some of them, for instance, KCl, NH_4Cl and RbCl are known to exhibit the so-called negative viscosity.

Together with the change of viscosity with temperature, the variation in relative viscosity (η_e/η_w where η_e is the viscosity of the electrolyte and η_w that of the water) has also been studied with regard to change in concentration and temperature with a view to see if the parallelism, drawn by Rabinovich (J. Am. Chem. Soc., *44*, 954; 1922) between the relative viscosities, at 25°C. of salts with common anions, and the hydration numbers of cations, can be extended to other concentrations and temperatures also.

Experimental.

Incidentally, a simple viscometer, suitable for relative measurements of viscosity and having very small or no kinetic energy correction has been evolved. Also some improvements have been made in the thermostat in respect of effective circulation of air to ensure uniformity of temperature at all points inside the thermostat. Densities, of the solutions used, were accurately measured at all the temperatures.

The temperatures chosen varied between 30° and 75°C. It was found, during preliminary experiments, that at temperature higher than this, the concentration of the solution altered considerably by evaporation; the highest temperature at which viscosity was determined had necessarily to be limited to about 75°C.

The concentrations studied for each of the eight electrolytes were N, N/2, and N/4, where N represents one gram equivalent of the salt, dissolved in 1000 grammes of the solution. To obtain

normal solutions, some workers, *e.g.*, Grüneisen (loc. cit.), Bousfield and Lowry (Phil. Trans., *A204,* 253 ; 1905), Simon (Compt. rend., *176,* 423 ; 1923), Herz and Martin (Z. anorg. Chem., *132,* 41 ; 1924) and others, dissolved one gram equivalent in a litre of solution. Normality by volume of the solvent makes their data unsuitable for general use, since the temperature at which solutions were made has to be stated with an accuracy to about 0·1° C., and also as some salts like NaCl, KCl, NH_4Cl and others, when dissolved in water produce a contraction. This contraction depends on the nature of the salt and the temperature at which the solution is made. Heats of solution and dilution also will have then to be taken into account.

Limits of applicability of the work done.

It will be observed, that, throughout the work, care has been taken to see that the limitations, imposed by Poiseuille's formula have not been over-ridden and similarly, as a very low pressure head has been used throughout, the range of Reynold's number, within which work has been carried out, is very small and the critical velocity has not been exceeded anywhere. The capillary of a fairly large bore was used together with small pressure heads. This, together with the lengths of the capillaries selected, made the kinetic energy correction quite negligible though not numerically zero. (The ratio of length to radius of the capillary varied from 350 to 450).

(B)

EXPERIMENTAL

Introductory.

The problem of the accurate determination of coefficients of viscosity is less complex when it reduces itself to making relative measurements. Since accurate values are available for the coefficients of viscosity of liquids like water, there is no special advantage to be gained by attempting to determine the viscosities of electrolytes and their temperature variation in an absolute manner.

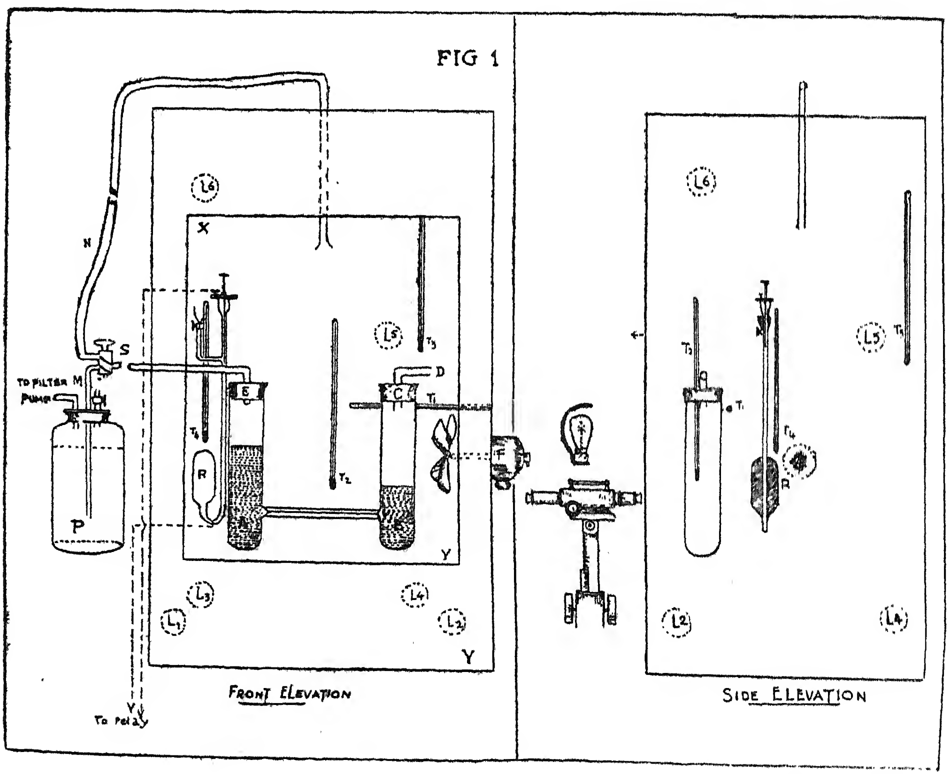
In respect of relative measurements, it has been pointed out by Applebey (J. Chem. Soc., *103,* 2167 ; 1913) that while the absolute viscosity value for water, as determined by careful experimenters, shows a divergence of 0·3 to 1·0 per cent, it is possible to obtain the ratio of viscosity of aqueous salt solutions to that of water with a precision of 0·01 per cent. The greater precision of the relative measurements can be traced to the simplification of the apparatus and also to the avoidance of errors, inevitable in precise measurement of dimensions such as length and radius of the capillary and the errors arising from the end conditions of the capillary.

Thus relative measurements, being simpler to carry out and more precise, it was decided to take water as the liquid of reference and evaluate the viscosities of the electrolytes at different temperatures. The main reason that prompted the choice of water as the standardising liquid is that its viscosity and density at different temperatures, are accurately known and that the viscosities (η/density) of the liquids investigated were not far removed from those of water at different temperatures.

The Apparatus.

The apparatus consists mainly of a capillary-flow type viscometer AB (Fig. 1) enclosed in a thermostat with a large observation window in the front. The cylindrical reservoir 'B' is kept in communication with the air in the thermostat by means of an India-rubber cork 'C' and the bent tube 'D'. The reservoir A is connected to a two-way tap S, by which it can be connected to the filter-pump through the safety bottle P, or, alternatively to the air in thermostat by means of the tubing N.

FIG 1



Initially the liquid in the reservoir B is drawn into the reservoir A by connecting the latter to the filter pump. Then the reservoir A is put in communication with the atmosphere (air in the thermostat). The heights through which the level fell was read by means of a cathetometer, placed outside the thermostat in front of the reservoir A. The times of fall were measured by means of a stop-clock reading correct to 0·2 of a second.

The Viscometer and Viscometry.

The viscometer used was of the Thorpe and Rodger type. The design and the dimensions were decided upon, after several trials with different lengths and bores of the capillaries and different bores of the reservoir tubes. The instrument primarily consisted of two vertical cylindrical reservoir tubes of bore 1·27 cm., with a horizontal capillary tube, of the effective average bore of 0·039 cm. and of 13·964* cm. length, sealed on to them at about 2 cm. above the bottom. The lower portions of the reservoirs served as dust traps.

The two reservoirs were cut from the same glass tubing which was selected for its uniformity of bores. This uniformity was verified by examining the external and internal diameters of several pieces, cut from it, under a travelling microscope and also noting whether equal weights of mercury increased the height of the meniscus to the same extent. Throughout the measurements, the same reservoir was always connected to the suction pump, the other being always open to the atmosphere.

The need for cylindrical reservoir tubes of identical diameters and conditions of the walls cannot be too strongly emphasized. With identical bores, there are no drainage nor surface tension effects and no corrections to be applied. The advantage of having cylindrical reservoirs, instead of the spherical or cylindrical bulbs as used by Thrope and Rodger (Phil. Trans., *A185*, 397 ; 1894) or the base-to-base funnel type of bulbs of Bingham and White (Z. phys., Chem. *80*, 670 ; 1912), which are difficult to blow identically equal, lies in the

*Since the ends are conical, the length could not be measured by a microscope. It is therefore calculated from the formula

$\eta = (\pi\, g.r.^4 P.t.)/8\, Q.L.$ (Rieman. J. Am. Chem. Soc., *50*, 51 ; 1928)

where η = coefficient of viscosity.

g = gravity.

r = effective average radius of the capillary.

P = pressure head.

t = time of transpiration.

Q = quantity of liquid.

L = length of the capillary,

since the viscosity of water η is known and other quantities can be determined accurately.

fact that the hydrostatic pressure head can be determined with accuracy and without applying any corrections either for the shape or the size.

The capillary was selected for its straightness and the uniformity of bore. The bore selected must be as nearly circular as possible, since, otherwise, the assumption of laminar flow, as postulated by Poisenille, is incorrect. To confirm this, the lengths of diameters at right angles were measured. The diameter selected was large enough to make the effect of obstruction to flow by dust particles, which occasionally find lodgment in the capillary, negligible.

The length of the capillary was, as has been stated, 13·9 cm. It was sealed to the reservoirs, thus avoiding the rubber or ground-glass joints, so unsuitable for work at temperatures above 40°C. While sealing, the change in diameter at both the ends of the capillary was made as gradual as possible to prevent eddy currents. Their slope too was made symmetrical by blowing conical glass joints as identical as the experimental skill would permit. The uniformities of the end portions of the capillary and of the conditions of flow in the wider cylinders to and from which it leads, were tested by taking a set of readings with the positions of the reservoirs interchanged, when no difference was noticed in the time of transpiration.

Since, in these experiments, only the hydrostatic pressures, caused by the difference in levels in the two reservoirs, are used, all the complications of external pressure arrangements and the air-tight joints involved are completely eliminated.

As the capillary of the viscometer was horizontal though not so long as to make the instrument somewhat fragile and awkward in shape, accurate levelling was necessary in order to make the hydrostatic head perfectly reproducible. This was secured by clamping the reservoirs in position to fixed iron stands, forming a rigid frame. Before every observation was recorded, the liquid meniscuses in the reservoirs were ascertained to be in the same horizontal line and the capillary horizontal by means of a cathetometer.

With the present "gravity" type viscometer the density of the liquid (the hydrostatic head of which produces the flow in the capillary) must be determined accurately, in order to calculate the relative viscosity.

As has been noted, no external pressure was used. As the pressure difference between the two reservoirs was small, the capillary need not be of small diameter, as is necessary, when high pressure-differences are employed, in order to reduce the so-called kinetic energy correction to a specified limit. Small diameters, necessary in other instruments, increase obstruction to flow on account of dust-

particles. Such obstructions are the basic cause of the want of concordance among the results of many authors and moreover, unless the velocities are very high, are not always avoidable.

Thus, it will be seen, that the present viscometer is designed to yield accurate results and is particularly useful, when relative measurements are made, as the kinetic energy correction becomes negligible.

THERMOSTAT

An adjustable thermostat for all temperatures between 30°C. and 80°C. :—

As the temperature at which the coefficients of viscosity of different electrolytes were to be determined, varied between 30° and 75°, an air-thermostat was prepared which controlled temperature with an accuracy of $\pm 0{\cdot}05°$ C. This was considered sufficient for the purposes of these experiments.

The apparatus took eventually a form, the general arrangement of which will be evident from Figure 1.

A dealwood, rectangular box (84 cm. × 53 cm. × 50 cm.) with walls 2·5 cm. thick and lined inside with a thick sheet of tin, was used as the thermostat cupboard. The minute crevices and slits between two planks were completely filled with putty and plaster of paris, which served the purpose fairly well within the range of temperature. The door was provided with a big glass window, "X Y". It moved on two hinges and in order that it should fix tightly on to the walls of the cabinet, the edges of the walls were provided with a coating of thick felt, thereby ensuring complete thermal insulation.

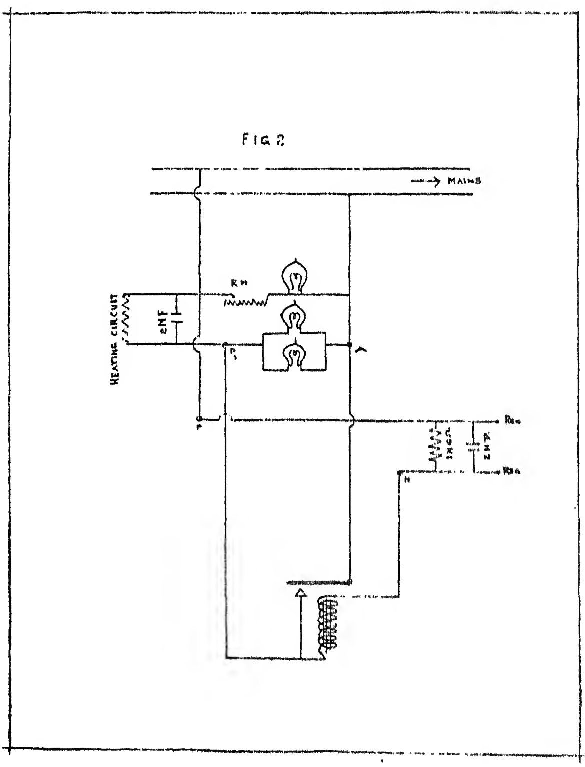
The thermostat was placed on a laboratory table. 60 Watt carbon filament lamps were used for heating the air inside. The number of lamps switched on, varied according to the magnitude of the temperature required. For temperatures between 30° and 45° C., only two lamps were used, while for temperatures upto 65°C. four were used, and for temperatures over 65°C. two auxiliary lamps (L_3, L_4 in Fig. 1) operated by a switch outside were used. The four lamps (L_1, L_2. and L_5, L_6), controlled by the relay outside, normally worked in unison. The distribution of the heating lamps was such that one of them was close to the regulator. This condition appeared necessary lest there might be some lag in the action of the thermo-regulator and consequent reduction in the sensitiveness of the thermostat. This precaution was taken in addition to the vigorous stirring.

Efficient circulation of air within the chamber was effected by means of a pycnometer, while at higher temperatures the specific of the fan were inside the thermostat. This arrangement prevents

change in temperature in the thermostat due to the heat developed by the motor on running for a length of time and avoids interference with the heating system inside. The fan in the above layout was so arranged that the air currents started by it were reflected by the walls on all the sides, so that air was brought into rapidly recurring contact both with the heating lamps and with the regulator, and thus a constancy of temperature in the thermostat was maintained over a very wide space.

The heating lamps, after several trials were so located that "dead" spaces were eliminated.

The heating circuit, the special regulator and the D.C. relay (Siemens-Schuckert, 200-250 Volts) were arranged as shown in the Fig. 2.



The thermo-regulator was of the usual shape, minus the horizontal appendage wherein the movement of a screw or a cap adjusts the level of the mercury meniscus. The regulator consisted of a large bulb, 2·5 cm. in diameter, connected to a capillary tube of 1·8 mm. bore. The bulb was filled with dry toluene, free from thiophene, and which had been previously kept in contact with freshly

distilled mercury for a sufficiently long time, and redistilled over sodium. Over the toluene and in the capillary, dry clean mercury was filled in the usual way. The funnel tubing in the side branch was left empty and the stop-cock open. The regulator was calibrated for different temperatures and the positions of the mercury meniscus noted on the stem. Instead of the cumbrous adjustment of the level of mercury by manipulating stop-cock in side-tubes, the nichrome wire, by means of a long screw attached to it, was lowered or raised, at will, to the position where the mercury level was expected for the required temperature. Thus the regulator could be set for any desired temperature within the range.

The insulated nichrome wire moved vertically in the capillary and was connected to one pole of the relay, while a platinum insertion in the capillary below was connected to the opposite pole. The sparking at the make-and-break between the wire and the mercury head was greatly minimized and a sharp response obtained, partly by reducing the current in the magnetic circuit to the minimum necessary to energize the relay and partly by placing a condenser, 2 MF capacity, across the regulator terminals. A similar condenser was also placed across the heating circuit terminals of the relay. In parallel with it, was put another high resistance (1 Megohm) in order to get rid of the inductive effective at the time of the break of the circuit. With this electrical arrangement, the relay worked for over a year without giving any trouble.

An important feature of the apparatus is the rapidity and ease with which it could be brought from a state of being at the room temperature and at rest, to performing its functions with precision and reliability.

The object of providing a large thermostat which could readily be adjusted for any temperature between 30° and 80° and maintained constant was thus achieved.

(C)

THE EXPERIMENTAL TECHNIQUE AND THE PREPARATION OF SOLUTIONS

Some errors and the precautions that were taken to avoid them :—

The viscometer was first cleaned with distilled water and kept filled with a strong solution of chromic acid for over twenty-four hours. It was then washed carefully with dust-free distilled water and allowed to drain for some time. Next it was rinsed with pure dry alcohol and dried by drawing through it a rapid current of air which was filtered through a thick wad of cotton wool. After this preliminary drying, it was transferred to a hot air oven where it was kept at a temperature over 125°C. for some hours.

This process of cleansing and drying was repeated every time a fresh measurement of viscosity was made either of water or an electrolytic solution.

All the beakers, pipettes, funnels, etc., used in the experiments were similarly cleaned and every thing that went in the viscometer was ascertained to be dust-free. The viscometer was kept inverted, when not in use.

Errors from the Non-Uniformity of the Diameter of the Reservoir :—

For every measurement only 25 cc. at 30°C. of the solution were put into the viscometer by means of a pipette which was kept specially for that purpose. This secured the same mean-level of the liquids for all the measurements at the same temperature thus, eliminating the errors that might arise from want of uniformity of the diameter of the reservoir tubes. Similarly, the viscometer was always in the same position and the height to which the liquid was raised was also the same.

Rushing in of the cold air and the condensation of water vapour :—

After the liquid was put into the viscometer, it was allowed to stand for over 30 minutes in order that all the disturbances caused during the pouring of the liquid should have ceased and that it should attain the temperature of the thermostat.

When the liquid was drawn up in the limb A by connecting it to the filter pump, the pressure above the liquid was less than that of the atmosphere and when it was again put into communication with outside air, the cold air which rushed in set up convection currents in the liquid. The agitation set up by the cold air from outside the thermostat vitiated the result to a certain extent. This was entirely prevented by turning the tube N (Fig. 1) inward so that it communicated with the thermostat air and not with outside air.

Before actually commencing to take time readings, the sucking of the liquid in 'A' and allowing it to fall again to the mean-level was repeated not less than three times so that at the commencement of taking readings, there was no trouble due to cool air in the tubing N joining the stop-cock to the thermostat. This precaution was found necessary, as in the preliminary experiments, it was noticed that the time of flow after the first suction was at times higher by 0·5 to 1·0 second than that obtained on a fourth or fifth repetition. This treatment partially obviated the possibility of a change in concentration due to evaporation as the viscometer was connected to the filter pump through the safety bottle P, containing water and the air above the solution was saturated with the vapour from the solution.

The cool air rushing into the apparatus from outside the thermostat caused yet another trouble at higher temperature, *viz.*, the formation of small drops on the walls of the reservoir 'A' due to the condensation of the water vapour from the liquid. The decrease in the liquid caused by these drops meant alteration of the mean level and therefore of the pressure. The device of making the tube open into the thermostat instead of outside removed this trouble also. The mean level of the liquid in the viscometer was always checked after completing a set of readings for every temperature, when, even at the highest temperature, no appreciable difference in the initial and final reading of the mean level was noticed.

Measurement of pressure.

With the above precautions, the liquid in the reservoir A was sucked up to a higher level by connecting it to the filter pump by turning the tap S. After it had reached a level, much higher than the one from which the measurements of the time of fall were taken, the tap S was turned to allow the thermostat air to get into the reservoir through the tube N. The cathetometer was adjusted for 20 mm. above the mean level and the time required by the level to fall was read out on a stop-clock, started exactly when the meniscus just touched the cross wires of the telescope. The different levels, at which the time of fall was recorded, were 20, 10, 5, 3, 2 and 1 mm. from the level respectively. The mean of a large number of observations was taken.

Measurement of the time of flow.

The time of flow, in the experiments, varied from 100 to 240 seconds and was measured by a stop-clock, periodically checked with another stop-watch. It was found to be sufficiently constant for the present purpose and time could be read to 0·2 second. The error, for the shortest period at the highest temperature for the least viscous solution, thus comes out to be less than 0·25 per cent.

Care was taken to ensure that the positions of the meniscus, passing the cross wire, were generally well illuminated, so that the events, being timed, should be identical.

Measurement of density.

The density of the solution investigated was found by means of two specific gravity bottles with capillary necks of capacity 10 and 25 cc. each, and, taking the mean of the two values obtained from each of them. The specific gravity bottles were filled with the liquid and kept in the thermostat for over 30 minutes. When all the extra volume of the liquid had overflowed they were taken out, allowed to cool, washed clean from outside with distilled water,

dried and weighed. Each of the two bottles was calibrated by determining its capacity at every temperature, calculated by dividing the mass of water (required to fill it at the temperature) by the density at that temperature obtained from Landolt and Bornstein tables. The densities of the solutions at different temperatures were then calculated by dividing the weights of the solutions by the capacity of the density bottles, as calibrated with water.

In the experiments below 45°C. densities were measured by means of a pycnometer, while at higher temperatures the specific gravity bottles were employed.

The values of density thus obtained were correct upto fourth significant digit and are sufficiently accurate for the purposes of these investigations.

Calculation of the Coefficient of Viscocity.

Thus knowing the times of flow and the densities of water and the solution, the relative viscosity of the solution is given by:

$$\frac{\eta_e}{\eta_w} = \frac{\zeta_e}{\zeta_w} \times \frac{t_e}{t_w}$$

(Hatschek, The Viscosity of Liquids, p. 27) where η_e & η_w, ζ_e & ζ_w, t_e & t_w, are respectively the coefficient of viscosity, density, corrected to vacuum and time of flow of the electrolyte and water), provided the heights of the level of the liquid remained the same in both the measurements.

Preparation of the solution.

All the salts used in these investigations were E. Merck's extra pure.

In the case of $BaCl_2$, a drop of HCl had to be added to the solution in order to remove the slight turbidity which is always obtained in solution of pure $BaCl_2$ in pure water.

$CaCl_2$ could not be obtained in the crystalline state, as it is hygroscopic. A solution of $CaCl_2$ was made by adding a quantity of redistilled water. And the Ca in the solution was estimated volumetrically by the oxalate method. Knowing the quantity of Ca, and therefore of $CaCl_2$ in this solution, the volume of water required to be added to it was calculated for different strengths, and the solutions made accordingly.

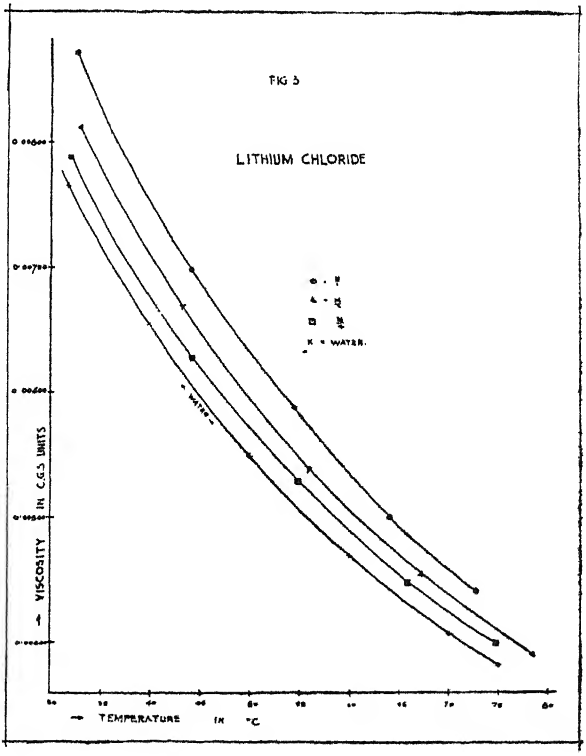
Measurements of the coefficient of viscosity at temperatures between 30° and 70° were made on the following salts :—

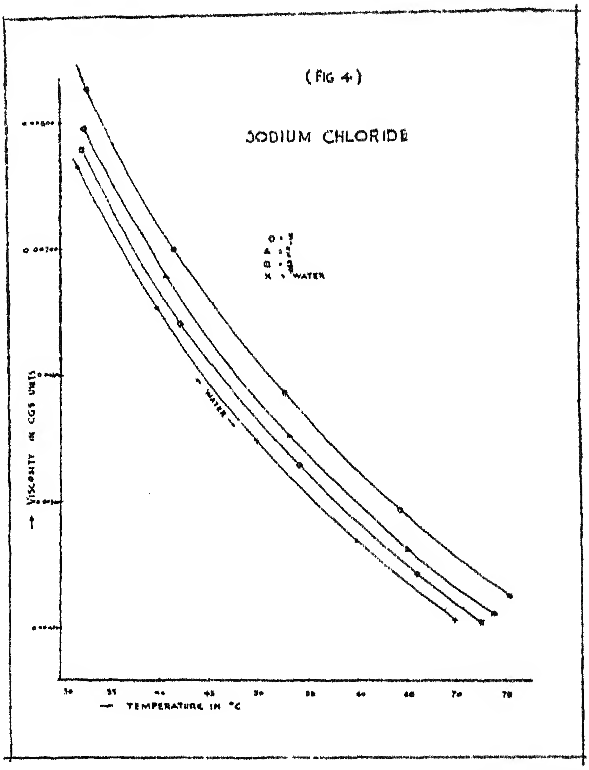
1. Lithium Chloride.
2. Sodium Chloride.
3. Potassium Chloride.
4. Rubidium Chloride.

5. Ammonium Chloride.
6. Calcium Chloride.
7. Strontium Chloride.
8. Barium Chloride.

With each salt at least three concentrations, *viz.*, N, 0·5N, and 0·25N were studied. The accompanying tables from I to VIII contain the results in a tabulated form. In column 3 the values of density as actually measured are also entered. The fourth column contains the relative viscosity as compared with water. This ratio has been given here with a purpose, in addition to the absolute viscosity as calculated in column 5 because it is required in the discussion on the question of negative viscosities.

The same results are shown in the form of graphs, Figs. 3-10. The peculiarities are accounted for in the section under Discussion. The curve for water has been shown in each figure for the sake of comparison.




(FIG 4)
SODIUM CHLORIDE
WATER
VISCOSITY IN CGS UNITS
TEMPERATURE IN °C

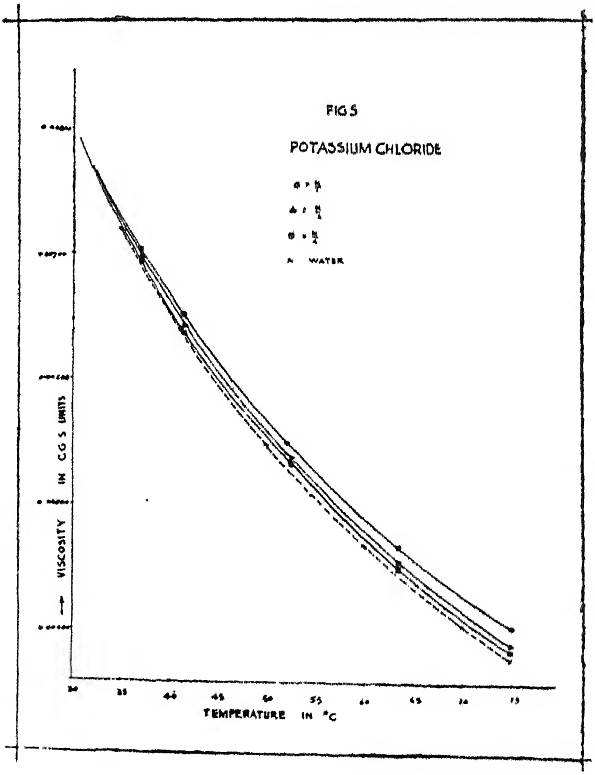


FIG 5
POTASSIUM CHLORIDE
WATER
VISCOSITY IN CGS UNITS
TEMPERATURE IN °C

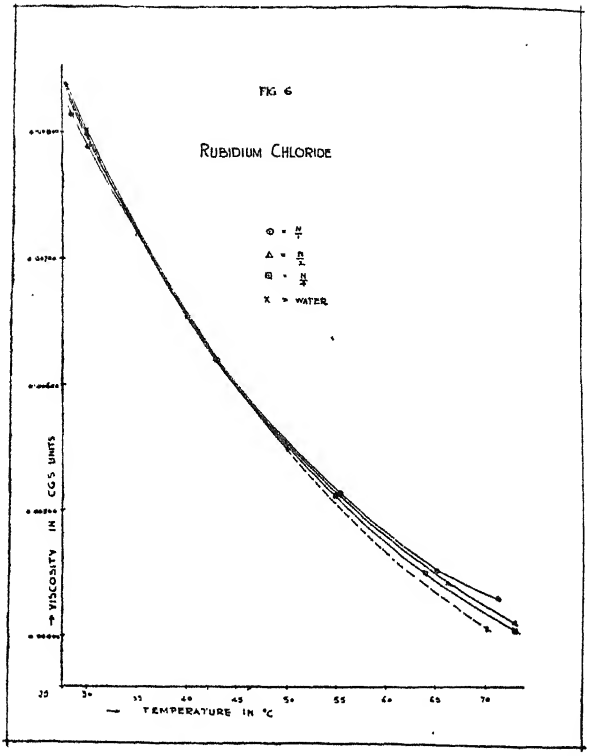


FIG 6
RUBIDIUM CHLORIDE
X = WATER
TEMPERATURE IN °C
VISCOSITY IN CGS UNITS

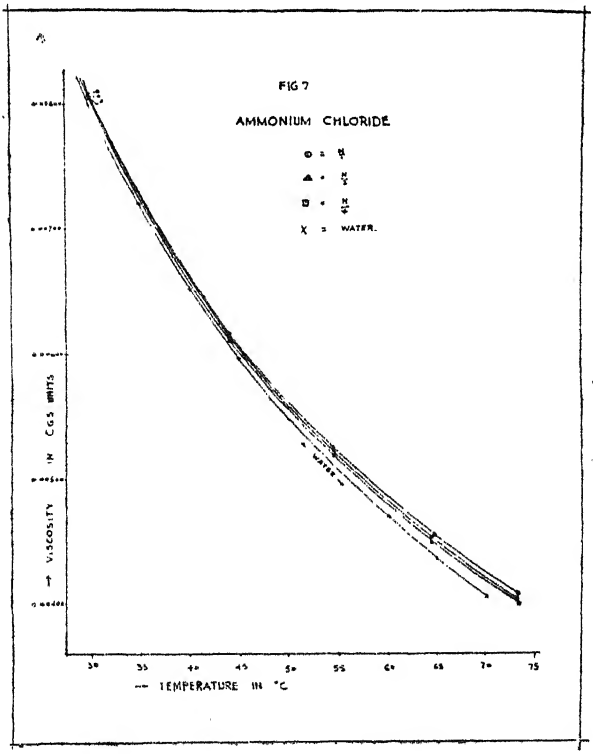


FIG 7
AMMONIUM CHLORIDE
X = WATER.
WATER
TEMPERATURE IN °C
VISCOSITY IN CGS UNITS

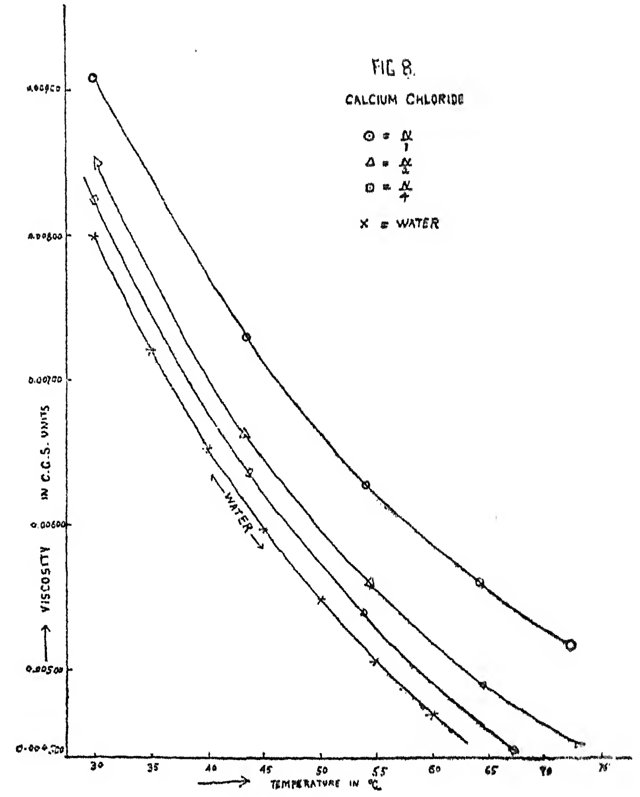


FIG 8.
CALCIUM CHLORIDE
O = N/1
Δ = N/2
□ = N/4
X = WATER
VISCOSITY IN C.G.S. UNITS
TEMPERATURE IN °C
WATER
0.00800
0.00700
0.00600
0.00500
30
35
40
45
50
55
60
65
70
75

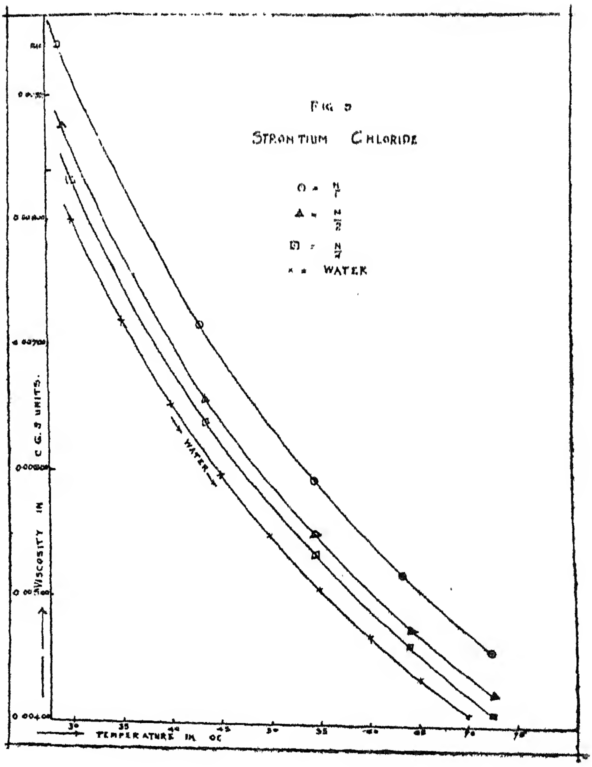


FIG 9
STRONTIUM CHLORIDE
WATER
VISCOSITY IN C.G.S UNITS.
TEMPERATURE IN °C

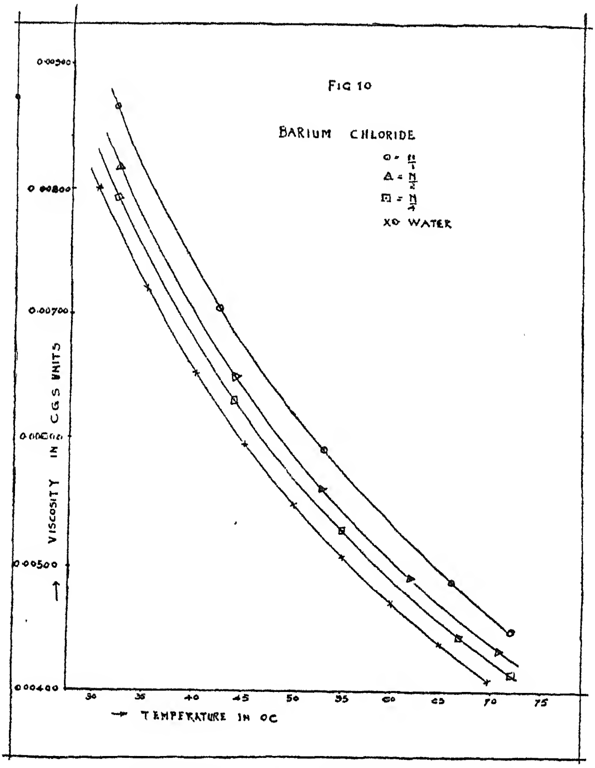


TABLE I. (i) *Lithium Chloride.*

(N=gm. equivalent in 1000 gms. of solution).

Concentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electrolyte.}}{\eta \text{ Water.}}$	η Electrolyte in C.G.S. units.
1·00 N.	32·8	1·019	1·156	0·00872
	44·0	1·015	1·161	698
	54·5	$1·010_5$	1·148	587
	64·4	1·005	1·137	500
	74·0	1·000	1·141	440
0·50 N.	33·0	1·007	1·079	0·00812
	43·7	1·004	1·088	666
	56·1	0·997	1·080	538
	67·3	0·991	1·070	452
	78·5	0·985	1·072	390
0·25 N.	32·3	1·001	1·033	0·00787
	44·3	$0·996_5$	1·037	627
	55·0	$0·991_5$	1·038	526_5
	66·0	0·986	1·036	446
	74·7	0·982	1·044	399

TABLE II. (ii) *Sodium Chloride.*

(N= gm. equivalent in 1000 gms. of Solution).

Concentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electrolyte.}}{\eta \text{ Water.}}$	η Electrolyte in C.G.S. units.
1·00 N	33·0	$1{\cdot}035_5$	1·103	0·00828
	41·7	1·031	1·108	699
	52·8	1·026	1·115	586
	64·4	1·021	1·122	494
	75·4	1·014	1·127	427
0·50 N.	32·7	1·015	1·049	0·00796
	40·7	1·012	1·053	679
	53·1	1·007	1·057	553
	65·0	1·001	1·060	463
	73·6	0·997	1·062	412
0·25 N.	32·4	1·005	1·025	0·00780
	42·5	1·001	1·027	641
	54·2	0·996	1·028	528
	66·0	0·991	1·030	443_5
	72·6	0·987	1·031	405

TABLE III. (iii) *Potassium Chloride.*

(N= gm. equivalent in 1000 gms. of Solution).

Concentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electrolyte.}}{\eta \text{ Water.}}$	η Electrolyte in C.G.S. units.
1·00 N.	30·0	1·042	1·005	0·00803
	41·5	1·038	1·026	652
	52·2	1·032	1·038	551
	63·5	1·026	1·049	468
	75·0	1·017	1·061	404
0·50 N.	30·0	1·020	1·002	0·00802
	41·5	1·016	1·012	643
	52·5	1·012	1·018	540
	63·5	1·007	1·024	457
	75·0	1·001	1·029	392
0·25 N.	30·0	1·008	1·000	$0{\cdot}00800_4$
	41·5	$1{\cdot}004_5$	1·006	639
	52·5	1·000	1·010	536
	63·5	0·994	1·014	452_5
	75·0	0·987	1·017	387

TABLE IV. (iv) *Rubidium Chloride.*

(N= gm. equivalent in 1000 gms. of Solution).

Concentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electrolyte.}}{\eta \text{ Water.}}$	η Electrolyte in C.G.S. units.
1·00 N.	30·0	1·089	0·9850	0·00788
	43·6	1·083	1·005	615
	55·3	1·074	1·019	514
	65·0	1·063	1·034	452
	71·0	1·058	1·059	431
0·50 N.	30·0	1·040	$0{\cdot}999_8$	0·00800
	43·6	1·035	1·004	614
	55·1	1·030	1·013	513
	66·2	1·025	1·029	442
	73·0	1·021	1·052	411
0·25 N.	30·0	1·017	$0{\cdot}999_8$	0·00800
	43·0	1·014	1·002	620
	55·0	1·009	1·010	511
	64·1	0·993	1·024	454
	73·0	0·990	1·046	408_5

TABLE V. (v) *Ammonium Chloride.*

(N= gm. equivalent in 1000 gms. of Solution).

ncentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electroyte.}}{\eta \text{ Water.}}$	η Electrolyte in C.G.S. units.
1·00 N.	30·0	$1{\cdot}012_5$	1·007	0·00806
	44·0	1·008	1·016	617
	54·5	$1{\cdot}002_5$	1·029	526
	64·7	0·996	1·038	455
	73·2	0·990	1·048	409
0·50 N.	30·0	1·004	1·008	$0{\cdot}00806_7$
	44·0	0·998	1·013	616
	54·2	$0{\cdot}991_5$	1·020	524
	64·5	0·988	1·031	454
	73·3	0·983	1·041	405
0·25 N.	30·0	1·000	1·009	$0{\cdot}00807_4$
	44·0	0·994	1·011	614
	54·4	0·990	1·017	522
	64·4	0·986	1·026	451_5
	73·5	0·980	1·038	403

TABLE VI. (vi) *Calcium Chloride.*

(N= gm. equivalent in 1000 gms. of Solution).

Concentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electrolyte.}}{\eta \text{ Water.}}$	η electrolyte in C. G. S. units.
	30·5	1·039	1·150	0·00909$_5$
	43·6	1·033	1·191	731
1·00 N.	54·0	1·028	1·218	628
	64·4	1·021	1·274	560
	73·0	1·017	1·330	519
	30·5	1·018	1·075	0·00850
	43·5	1·012	1·080	662
0·50 N.	54·5	1·007	1·094	559
	64·5	1·002	1·114	490
	73·0	0·998	1·152	450
	30·5	1·011	1·029	0·00815
	43·5	1·006	1·133	643
0·25 N.	54·5	1·002$_5$	1·038	532
	64·5	0·997	1·040	462
	67·0	0·995	1·046	444

(N= gm. equivalent in 1000 gms. of Solution).

TABLE VII. (vii) *Strontium Chloride.*

Concentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electrolyte}}{\eta \text{ Water.}}$	η Electrolyte in C.G.S. units.
	29·0	1·066	1·150	0·00941
	43·0	1·060	1·155	714
1·00 N.	54·4	1·055	1·158	593
	63·4	1·050	1·162	519
	72·5	1·046	1·166	459
	29·0	1·030	1·071	0·00876
	43·5	1·025	1·073	658
0·50 N.	54·4	1·021	1·075	550$_5$
	64·0	1·016	1·075	476
	72·5	1·012	1·076	424
	30·0	1·011	1·038	0·00831
	43·5	1·006	1·042	639
0·25 N.	54·4	1·003	1·044	535
	64·0	0·999$_5$	1·044	463
	72·9	0·994$_5$	1·045	409

TABLE VIII. (viii) *Barium Chloride.*

(N= gm. equivalent in 1000 gms. of Solution).

Concentration.	Temperature Degrees Centigrade.	Density.	$\frac{\eta \text{ Electrolyte.}}{\eta \text{ Water.}}$	η Electrolyte in C.G.S. units.
1·00 N.	32·0	1·086	1·126	0·00864
	42·5	1·080	1·128	704
	53·0	1·076	1·130	592
	66·0	1·070	1·131	487
	72·0	1·066	1·132	448_5
0·50 N.	32·0	1·038	1·064	0·00816
	44·0	1·034	1·068	649
	53·0	1·030	1·070	560
	62·0	1·026	1·073	489_5
	71·0	$1{\cdot}021_5$	1·075	431_5
0·25 N.	32·0	1·017	1·033	0·00792
	44·0	1·011	1·037	630
	55·0	1·006	1·041	527
	67·0	$0{\cdot}999_5$	1·044	443
	72·0	0·996	1·045	414

DISCUSSION OF RESULTS

A. OBSERVATIONS FROM THE GRAPHS

It will be seen from the Tables, II to IX, and the graphs, Figs. 3 to 10, that of the eight salts studied, $BaCl_2$ and $SrCl_2$ alone give parallel $\eta - t$ curves for all three normalities; with $BaCl_2$ the fall in viscosity from N to N/2 is greater than that from N/2 to N/4; with $SrCl_2$, the fall from N to N/2 is nearly double that from N/2 to N/4.

With NaCl and $CaCl_2$, the curves show a tendency to converge at temperatures below 30°C.; the divergence at higher temperatures is less pronounced between N/2 and N/4 than between N and N/2. At about 70°C., the fall in viscosity between N and N/2 is almost double that between N/2 and N/4 for NaCl, while, it is, under the same conditions, more than twice as much with $CaCl_2$. Between

temperature 30° and 42°, N/2 and N/4 curves of both NaCl and $CaCl_2$ run parallel; while, at higher temperatures, N/2 and N/4 curves for NaCl continue to be parallel, those for $BaCl_2$ diverge. A remarkable divergence is noticeable, particularly at higher temperatures, between N and N/2 $CaCl_2$ curves.

The curves for LiCl are peculiar inasmuch as they show a tendency towards convergence at about 72° while they diverge on both sides of this temperature. In the direction of lower temperatures, the divergence is regular but, above 72°, the curve for N diverges more rapidly and suddenly from that for N/2 than does the N/4 curve. The divergence between N/2 and N/4 continues to be regular.

The graphs for KCl, RbCl and NH_4Cl, which are known to lower the viscosity of water, are more complicated. With KCl, the three curves converge at about 30°C. and diverge again at lower temperatures, inverting their order, a conclusion remarkably borne out by Simon's (Compt. Rendu, *176*, 437; 1923) data. It is also to be noted that the fall of viscosity between the three concentrations is very small compared with that obtained with any of the salts described above. The curves for N/2 and N/4 are close to one another while that for N/1 diverges a little more.

Similarly, with RbCl, there is a convergence (intersection of the lines) at about 40°C. The curves for N and N/2 merge upto 45°C., when they definitely separate. The divergence is small upto 65°C., after which there is a sudden deviation, comparable with that noticed between the N and N/2 LiCl curves near 72°. The divergence between N/2 and N/4 RbCl is practically uniform and begins at about 42·5°C. Like KCl curves, these curves also diverge again at lower temperatures. The lower normality then shows the higher viscosity.

With NH_4Cl, the curves for N/2 and N/4 almost merge, while that for N diverges slightly. These curves also show a point of convergence at about 32°C.

Thus, it will be seen that for KCl, RbCl and NH_4Cl, there seems to exist a critical temperature at 30°, 40°, 32° C., respectively, at which even a large change of concentration like that from N/4 to N has no effect on the viscosity, which remains equal to that of water. For these salts, the effect of change of concentration on the viscosity, at any of the temperatures studied, is much smaller than with the other salts. With these salts also, change in concentration appreciably alters the viscosity (relative viscosity) only above 50°. Below 30°, an increase in concentrations only lowers the viscosity, while, above 30°, it either does not alter the value or increases it.

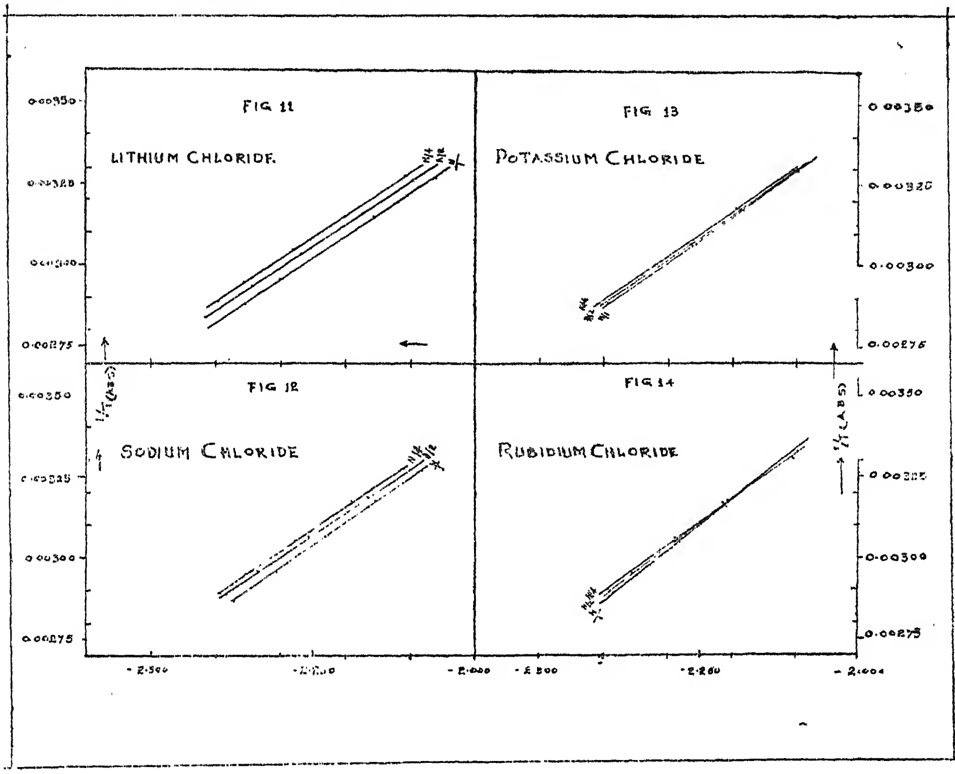


FIG 11
LITHIUM CHLORIDE
FIG 13
POTASSIUM CHLORIDE
FIG 12
SODIUM CHLORIDE
FIG 14
RUBIDIUM CHLORIDE
0·00350
0·00300
0·00275
0·00300

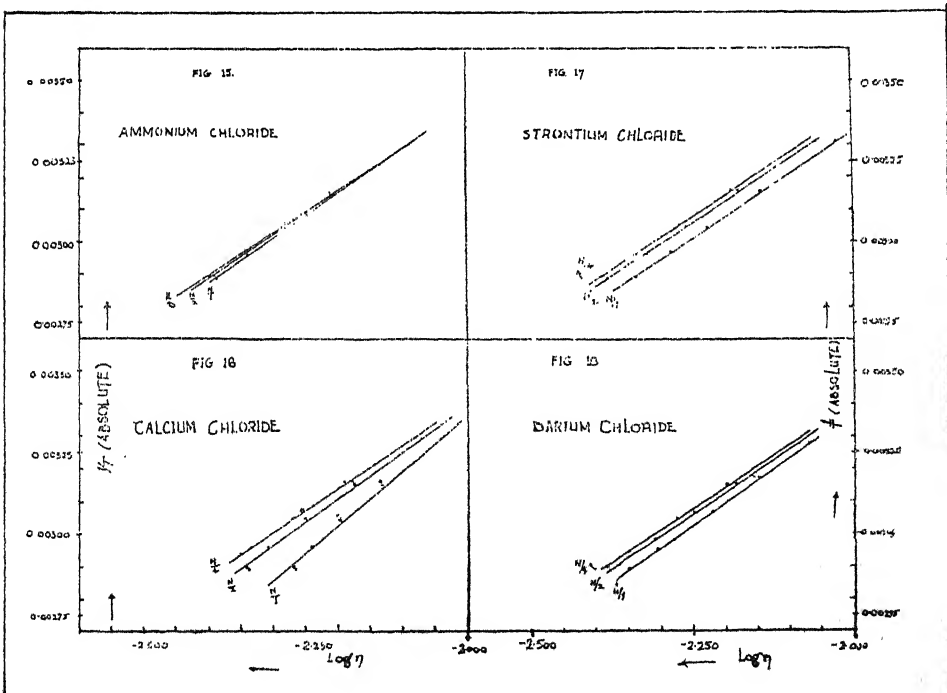


FIG 15.
AMMONIUM CHLORIDE
FIG 17
STRONTIUM CHLORIDE
FIG 18
CALCIUM CHLORIDE
1/T (ABSOLUTE)
FIG 19
BARIUM CHLORIDE
1/T (ABSOLUTE)
-2·500
-2·250
-2·000
Log η

B. THEORETICAL ASPECTS (QUALITATIVE)

The chief factors which appear to govern the viscosity of a solution are : (*i*) viscosity of the solvent, (*ii*) hydration of the solute particles or its ions, (*iii*) the electric field of the ions, and (*iv*) depolymerization of the solvent as well as of the solute particles.

In the solutions, studied in this paper, the solvent is water. Water exists in polymerised forms and ordinary water is supposed to be a suspension of large aggregates of H_2O molecules in a medium of less aggregated ones.

(*i*) *Viscosity of the Solvent.*

Water in itself shows a highly anomalous behaviour as regards the change of viscosity with temperature. At low temperatures it is slightly associated with large molecules and large viscosity, while at higher temperatures, it gradually comes to normal. [cf. deviations from the $\log\eta - 1/T$ straight line at temperatures lower than 60°C. Iyer (Ind. J. Phys., Vol. V, Part III, 373 ; 1930)].

(*ii*) *Hydration of the solute particles or its ions.*

The effect of hydration obviously will be to increase the viscosity of the solution. With highly hydrated salts, like those of Lithium and Sodium, the relative viscosity (η electrolyte $\div$ η water) is diminished by increase in temperature for certain temperatures, owing to thermal decomposition of the hydrates. This behaviour is contrary to the general rule for electrolytes. Hatschek (The Viscosity of Liquids, p. 122) does not consider the special case of the highly hydrated salts when enunciating the rule, that the increase in relative viscosity with increasing temperature distinguishes electrolytes from non-electrolytes. It is also known from the tables collected by Rabinovich (J. Am. Chem. Soc., *44*, 954 ; 1922) from the data of Reyher (Z. phys. Chem., *2*, 744 ; 1888), Kanitz (Ibid., *22*, 336 ; 1897) and Reisenfeld (ibid., *66*, 672 ; 1909) that for salts with a common anion, the highly hydrated cations increase to a large degree the viscosity of water in a normal solution, while the least hydrated diminish it. The order of hydration is as follows :—

$$Li > Na > \ldots NH_4 > K > Rb > Cs.$$

We may pursue this further. With an electrolyte at infinite dilution, we may assume that the friction R is purely hydrodynamic, since the individual ions, owing to their great distances apart, exert no electrostatic force on one another. At higher concentrations of course the frictional force will depend on the concentration, electrostatic forces then playing an important part. Consequently, the Stoke's formula, $R = 6\Pi\eta r$ (where R = frictional force, η = viscosity of the liquid, and r = ionic radius) which is only approximately cor-

rect, may be applied in determining the ionic radius. From fundamental considerations regarding the ionic mobility, we get :

$$u \sim 1/\eta r \approx (8{\cdot}15 \times 10^{-9})/\eta r \quad \ldots\ldots\ldots\ldots \quad (1)$$

where u is the ionic mobility (proportional to $1/R$). Hence in the same solvent the radius of the ion r is inversely proportional to u, the ionic mobility. If we consider now the ionic mobilities of different ions, we find that the ionic diameters are in the following order :

$$Li > Na > K \ldots$$

while their atomic diameters are undoubtedly in the reverse order. This can be explained on the assumption of hydration, *i.e.*, the ion—especially the Li ion—is surrounded by an envelope of water. According to Born (Z. Elektrochem. *26*, 401 ; 1920. Z. Phys. *1*, 221 ; 1920), hydration is not necessarily a chemical process but is a simple electrostatic effect, inasmuch as the water molecules, behaving as dipoles, are attracted by the ions of the dissolved electrolytes. The smaller the ion, the stronger is the effect on the solvent molecules and a greater number of them (solvent molecules) will be bound. This explains, why, when the true radius of Li ion is small, it is greatly increased by hydration.

The confirmation of the equation (1) is of practical importance, because, with it we can easily obtain the mobilities of ions in different solvents, following the treatment of Ulich (Fortschr. Chemic., *18*, 1926), Ulich and Birr (Z. angew, Chem., *41*, 443 ; 1928). As the true ionic radius can be determined from the grating measurements in the solid condition, we can draw conclusions from the difference between the apparent and the true radii, regarding the size of the hydration envelopes and the approximate number of the molecules of the solvent combined with an ion—the so-called solvation number. With water as solvent, Ulich obtains for Lithium and Sodium solvation numbers 7 and 4 respectively.

(*iii*) *The Electric field of the ions.*

The effect of the electric fields of the ions quite contrary to the assumptions of Euler (Z. physik. Chemi., *25*, 536 ; 1898) consists, as Applebey (J. Chem. Soc., *97*, 2000 ; 1910) pointed out, in the formation of temporary ionic lattices and manifests itself therefore in an increase in viscosity.

According to the ionic attraction theory of electrolytes, "the ions tend to build and maintain a space lattice structure in the solution and any influence tending to disturb this space lattice arrangement, whether by the heat motion of the solvent molecules, or by any relative motion on the part of the liquid, will be opposed by the inter-ionic forces". These forces tend to stiffen the solution or in-

crease its viscosity. Sutherland (Phil. Mag., VI, *14*, 1 ; 1907) suggests that the inter-ionic attraction should increase the viscosity of electrolytic solutions.

(*iv*) *Depolymerization of the solvent and the solute.*

Depolymerization (dissociation of molecular aggregates into simple particles) of the *solute* is brought about during the process of solution and ionization. The depolymerization* of the *solvent* is effected both by increased temperature and by increased concentration of the solute, as can be seen from the fact that increased concentration of the solute means decreased concentration of the solvent which therefore must increase depolymerization. For, with water, the volume of the polymerized molecule of water is greater than the sum of the volumes of the component molecules.

Another very important factor that may materially contribute towards depolymerization of the solvent is the hydration of ions. Traube (Phil. Mag., (6) *8*, 158 ; 1904), Blancord (J. Am. Chem. Soc., *26*, 1315 ; 1904) and Bousfield (Trans. Roy. Soc., *206A*, 101 ; 1906) showed this to be the consequence of the hydration of ions, if the law of mass action is applied to the equilibrium between the associated and non-associated molecules.

Depolymerization is rather the result of the decrease of water concentration due to solution, of hydration and, especially, with dissolved salts, of the high dielectric constant of the solute.

Tammann (Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen. Hamburg. 1907) considers that there is only one force (Binnen Druck) or internal pressure existing between the solvent and the solute, and he has attempted in a paper published in conjunction with Rabe (Z. anorg. Chem., *168*, 73 ; 1927) and also Tammann (ibid., *174*, 231 ; 1928) to relate the change in viscosity consequent on the dissolution of a salt in water with this pressure.

He took Bridgman's (Proc. Am. Aca., *61*, 57 ; 1926) results of the viscosity of water at various pressures and compared them with his own results of the viscosities of KCl, KBr, KI and NH_4Cl solutions of which the internal pressure was equal to the external pressure applied to the water. Tammann's experiments have not attracted much attention mainly because of the quantitative vagueness of the

*The disappearance of the maximum density phenomenon, when salts are dissolved, shows that the effect on the water equilibrium is a depolymerization. This effect, according to Sutherland (Phil. Mag., V, *50*, 481 ; 1900) will lead to a diminution of viscosity. The diminution will not, however, depend alone on the concentration of the ions, but also upon the amount of the polymeride present. The effect will therefore slowly decrease with successive additions of salts.

internal pressure. There is a large discrepancy observed between the values of internal pressures when calculated by two different methods (S. Hildrebrand—J. Am. Chem. Soc., *38,* 1458 ; 1916).

Rabinovich (J. Am. Chem. Soc., *44,* 958 ; 1922) points out that the relations described by Tammann can be better explained by the theory of depolymerization as this gives a simple and clear picture of the process, whereas Tammann's explanation is a purely formal description.

But, in any case, according to Richards and Palitzsch (J. Am. Chem. Soc., *41,* 59 ; 1919) viscosity must be considered to depend on the size of the molecules and their outward configuration more than on the "internal pressures" holding them together.

Of these factors, hydration and the electrical field are able only to increase, not to diminish, the viscosity of water. Only the depolymerization of the solvent, *i.e.,* of the component quantitatively prevailing in the solution and therefore materially affecting the viscosity, is able to produce by itself the so-called 'negative' viscosity, such as that displayed by KCl, RbCl and NH_4Cl.* But other factors can favour or hinder and in many cases over-balance its effect, giving rise to positive viscosity $(\eta_c > 1)/\eta_w$.

Thus for LiCl, NaCl, $SrCl_2$, $CaCl_2$, and $BaCl_2$, the factors which increase the initial viscosity such as the hydration of ions and electric fields of ions are dominant factors. In their case, the lowering of the initial viscosity of water, brought about by the necessary depolymerization (of water) is more than balanced by the increase in the viscosity due to hydration.

The initial steep nature of the $\eta - t$ curves for LiCl suggests that the degree of hydration is diminishing rapidly with increase of temperature. At higher temperatures, however, the degree of hydration has been reduced to a minimum, the depolymerization of water must also have advanced to a considerable extent and in the neighbourhood of normality 1, the inter-ionic forces seem to get upper hand, thus increasing divergence, unless the Li-ion begins to be hydrated again, which, however, does not seem to be very probable.

---

*Wolkowa and Titow (Z. phys. Chem., *A155,* 51 ; 1931), working on "viscosity isotherms and the differential heats of dilution of aqueous solutions" suggest that an aqueous electrolytic solution has a negative heat of dilution, when it exhibits the 'negative viscosity'. It may further be pointed out that Wüst and Lange (Z. Elektrochem., *30,* 353 ; 1924) find, for the variation of the heat of dilution with concentration, similar results. The heat of dilution for KCl upto a certain concentration becomes increasingly negative with increasing concentration, though the heat of solution, at the same time, becomes increasingly positive.

The parallelism, drawn by Rabinovich (loc. cit.) between the η_c/η_w for normal solutions of different salts with common anion, and the hydration numbers of their cations, usually holds good for other temperatures and strengths, where Li is the more hydrated cation than Sr. Similar relationships for different concentrations and temperatures are also to be found among $CaCl_2$, and $BaCl_2$, though the hydration numbers of their cations are not available.

With KCl, RbCl and NH_4Cl, however, the hydration numbers of the cations are much smaller than that of the anion Cl. Thus for these salts, the amount of water bound up by these ions is much smaller than that with the other salts. Consequently the increasing effect on viscosity is much less than with other salts, while the decrease due to depolymerization is almost normal. The viscosities, at different concentrations, depend upon the mutual depolymerization of the electrolyte and the solvent (*i.e.* water), and that the resultant behaviour depends on the temperature. At low temperatures, where a large proportion of trihydrol is present, the addition of the electrolyte breaks up some of the ice molecules. A further addition of the electrolyte, upto a certain concentration, causes the breaking of an increasing number of ice molecules and therefore an increasing diminution in viscosity. This shows how, upto a certain concentration and within a certain temperature range, any of these salts, (as also Cs) can actually lower the viscosity of water.

C. SEMI-EMPIRICAL FORMULÆ FOR VISCOSITY

We now turn to discussion of the semi-empirical formulæ which have been developed to represent viscosity values in regions in which theory cannot be applied. They deal with the variation of viscosity with temperature. Porter (Phil. Mag., VI, *23*, 458 ; 1912) showed that viscosities should be capable of being represented by a formula of the type $f\ (\eta)\ A + B/T$. He deduced this form from the fact that the reciprocals of absolute temperatures at which two liquids have equal viscosity are linearly related. The general theory of rule of this type has been developed by Wheeler (Phil. Mag., VII, *12*, 685 ; 1931. Phys. z., *32*, 674 ; 1931).

Raman's formula.

In order to explain the viscosity paradox, namely, the decrease of the viscosity of liquid with increasing temperature, in contrast to the increase of gaseous viscosity with increasing temperature, Raman (Nature, *111*, pp. 532, 600 ; 1923) put forward a theory of liquids based on their observed behaviour in respect of light-scattering and X-ray diffraction. It envisages the transport of momentum through a liquid, as taking place in two distinct ways, partly by the transverse

elastic waves, as in a solid, and partly by the diffusion as in gas molecules; the latter process is comparatively slow. His hypothesis postulates the existence of two types of molecules in the liquid state; that is, the liquid state of aggregation is composed in part, of molecules rigidly attached to each other as in a solid or crystal and, in part, of molecules, relatively free, as in a gas. The effective rate of the transference of momentum in the liquid depends on the proportion of these two types of molecules and is greater in a liquid than in the vapour, at the same temperature and pressure, in the ratio of $e^{\frac{E_2}{RT}} + e^{\frac{E_1}{RT}}$ where E_2 and E_1 are the energy terms involved in separating molecules of the vapour and crystalline types respectively. The viscosity of the liquid is therefore given by the formula

$$\eta \text{ liquid} = \eta \text{ vapour} \times e^{\frac{E_1 - E_2}{RT}} \ldots\ldots (1) \text{ IIID}$$

since $E_2 > E_1$, it follows that the viscosity of the liquid will diminish with rising temperature.

Raman suggests the equation

$$\eta \text{ liquid} = A\, e^{\frac{B}{T}} \ldots\ldots\ldots\ldots\ldots\ldots (2) \text{ IIID.}$$

where A and B are two constants.

This simple exponential formula is remarkable inasmuch as two constants suffice to express the change of viscosity with temperature over the range between freezing point and boiling point. Moreover the constants are not quite arbitrary but, (cf. equations 1 and 2) have a physical significance. A is comparable to η_{vapour} and from the argument used in deducing the formula (1), B is of the same order of magnitude as W/R where W is the molecular latent heat of fusion and represents the heat quantities involved in the alterations of special orientation (cf. Drücker, Phys. Chem. *92,* 181, 1918), and R = 1·985. Iyer (Ind. J. Phys., Vol. V, Part III, 373; 1930) discusses at length the physical significance of A and B.

Porter's function (Phil. Mag., VI, *23,* 458; 1912).

$$f(\varphi) = (K/T) + C$$

becomes identical with Raman's formula if $f(\phi) = \log(\phi)$ where ϕ is the fluidity of the liquid. Drücker (Z. phys. Chem. *92,* 281; 1918) proposed a similar formula and it may be written as

$$\frac{d}{dt} \log \phi = W/RT^2 \ldots\ldots\ldots\ldots\ldots\ldots (3) \text{ IIID.}$$

With aqueous solutions of strong electrolytes, straight lines are obtained. For each curve mean values of A and B can be deduced.

The values of the constants are found not to be so precisely defined as they are by Raman.

It is clear from the values of B that most of the solutions give lines approximately parallel to that given by water and that the lines for different normalities of the same salt are closely parallel. The constant A in his case varies with the salt used and usually decreases with the normality of the solution. It is of the same order as the value of A for water. There is no relation to the viscosity of steam. Iyer (loc. cit.) has of course pointed out that the theory need not be expected to apply with any great accuracy to the highly associated liquids of the water type.

TABLE XVIII.

Raman's formula. $A. e^{B/T}$.

	$A \times 10^7$	B
Water (Iyer)	206·0	1822.
Water (Author)	220·0	1790.

Electrolyte.	Normality.	$A \times 10^7$	B.*
LiCl	N/1	285	1455
	N/2	280	1463
	N/4	273	1477
NaCl	N/1	426·6	1610
	N/2	402·7	1619
	N/4	393·6	1620
KCl	N/1	595·7	1472
	N/2	595·7	1472
	N/4	595·7	1472
RbCl	N/1	363	1615
	N/2	363	1615
	N/4	363	1615
NH_4Cl	N/1	385	1621
	N/2	385	1621
	N/4	385	1621
$CaCl_2$	N/1	595·7	1525
	N/2	412·0	1623
	N/4	389·0	1623
$SrCl_2$	N/1	335	1706
	N/2	302	1722
	N/4	302	1722
$BaCl_2$	N/1	426	1610
	N/2	346	1661
	N/4	328	1667

*Iyer (loc. cit. p. 377) points out that "a difference of 30 to 40 units in the value of 'B' does not very much affect the slope of the curve drawn, since 'B' appears in the terms $e^{\frac{B}{T}}$

Andrade hypothesis.

Andrade (Nature, *125,* pp. 309, 582 ; 1930 ; *128,* 835 ; 1931) suggests the same formula as Raman's. He assumes that the transference of momentum between parallel-moving layers of the liquid is accomplished through the medium of temporary unions* between contiguous molecules. The union takes place under the action of the residual field of the molecules, which though sufficient to bind them permanently in the solid state, is overcome by the energy of motion in the liquid state. The greater the temperature agitation, the smaller the probability that the average residual field will result in temporary union of a given molecule. The viscosity of a liquid therefore decreases with rise in temperature until finally the energy of motion overcomes the molecular field and the liquid boils. The general picture is that of a "transitory and fluctuating crystallisation".†

The constant B of his equation which is a measure of the molecular field, is connected with the boiling point and also with the dielectric polarisation due to the deformation of the molecule and it is of the form $-E/K$, where E is the energy of juxta-position and K the Boltzmann constant. The formula assumes the frequency of impacts to be independent of temperature and it is therefore likely that the constant 'A' may depend slightly on the temperature, but is generally constant to a first approximation. At lower temperatures the formula does not fit well for water and other associated liquids. He therefore suggests that at higher temperatures the liquids are either not associated at all, or else that, such association, as may exist, is stable and unaffected by temperature. He therefore adds a third constant to his formula (same as (2) III.D) which has the form $\eta = A'. e\ (B'/T - \theta)$ and suggests yet one more formula of the type

$$\eta = A\left(1 + \alpha e^{-\beta T}\right) e^{\beta T} \qquad \text{(4) III. D.}$$

the term $1 + \alpha e^{-\beta T}$ expressing the decrease of association with tem-

*Regarding temporary union of the molecules as postulated by Andrade, it may be of interest to note Langmuir's view that "atoms of tungsten, molybdenum, and platinum striking a clean dry surface in his vacuum are condensed as solids at the first collision" and "have a certain average 'life' on the surface" and to Maxwell's statement that "the collision between two hard spherical balls is not an accurate representation of the encounter of two molecules. A better representation will be obtained by supposing the molecules to act on one another in a more gradual manner so that the action between them goes on for 'a finite time'." This 'finite time' of Maxwell's and Langmuir's 'life' of chemical union may well be compared with Andrade's 'temporary' unions.

†Sato (Sci. Rep. Tohoku. Univ., *14,* 403 ; 1925) suggests "a fibrous structure of the molecules in a viscous fluid in motion".

perature. The equation (4) has four constants, α, β, A and B and is more or less empirical.

Expressions similar to Raman's have been proposed by Drücker (Z. phys. Chem., *92*, 181 ; 1918), Dunn (Trans. Farad. Soc., *22*, 401 ; 1926), Sheppard (Nature, *125*, 489 ; 1930), J. Rheology, *1*, 349 ; 1930), Stewart (Phys. Rev. *38*, 1575 ; 1931) and Ornstein (Z. Krystall., *79*, 90 ; 1931).

It will be clear from the above discussion that a lack of knowledge of the forces, acting in the liquid state precludes any accurate theory of the viscosity of the liquids. Semi-empirical formulæ of the type proposed by Raman fit the facts well but are based on qualitative rather than quantitative considerations.

With very dilute aqueous solutions, Falkenhagen's extension of the Debye-Rückel Theory enables us, to give an explanation of the irreversible mechanism involved in the viscosity phenomena exhibited by strong electrolytes, and, if the viscosity of water be assumed, to calculate the viscosity of these solutions.

Although a theory of more concentrated solutions of strong electrolytes and of weak electrolytes at all concentrations—the true degree of dissociation with them varies from 0 to 1—has been attempted many times the exact theory has not yet been developed. In such solutions, not only the electro-static forces (that is the Coulomb forces and the forces of polarization) are significant, but also the chemical or quantum-mechanics forces and the interionic dispersion forces are of great moment.

Since Falkenhagen refers to very dilute solutions, the author's results are of practical rather than of theoretical value. Nevertheless with progress of time it may become possible to extend theoretical calculations to the regions here investigated practically.

SUMMARY

1. A viscometer, suitable for relative measurements has been evolved, giving the kinetic energy correction quite negligible.
2. An air-thermostat has been constructed with improvements in the heating arrangements and air circulation.
3. The coefficients of viscosity of aqueous solutions of the chlorides of lithium, sodium, potassium, rubidium, calcium, strontium, and barium, and ammonium chloride have been determined between 30° and 75° for normalities N, N/2, N/4.
4. An account has been given of the present position of the theories of viscosity of electrolytic solutions, and, as far as possible, the results obtained have been discussed in the light of these theories.

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SOME INTERPRETATIONS OF THE BAND SPECTROSCOPIC RESULTS OF NITROGEN

BY

N. R. TAWDE.

1. *Introduction.*

In the case of band spectra of diatomic molecules, we are in possession of very extensive experimental material. The results derived from vibrational and rotational analysis of many diatomic molecules have found important applications in the hands of Mulliken, Birge, Kronig and many others. As a result of the work of these authors, the theory of the electronic bands of diatomic molecules is now almost complete. But many of the results in the case of individual molecules have not yet been put to rigorous theoretical treatment. It is in rare cases that the entire course of potential energy curves given by approximate expressions has received the claim of validity from experimental investigation. The calculation of dissociation energy by extrapolation upto the convergence limit of bands is not always reliable. Only in a few molecules, have the nuclear vibrations been studied upto the dissociation limit.

While investigating a graphical method of following the limit of convergence of vibration series in an electronic state, Rydberg* has found some interesting results in the case of certain molecules. It has been shown by him that the first differences (ΔG) in the vibrational levels are a function of the coefficient B_v of the rotational energy term. The significant result of Rydberg's investigation is that the constant of proportionality between these two quantities has been found to be the same for different electronic states of the same molecule with the exception of LiH and NaH. The result is expected to hold good generally as a consequence of the behaviour of most other molecules.

In order to see whether Rydberg's conclusions are valid, it is proposed to study in this paper a particular hypothetical case of N_2. This molecule has four excited states, the transitions between which give various well-known band systems. Consequently this molecule is suitable for an investigation of this type.

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*Rydberg, Zeit. f. Phys. *73*, 376, (1931).

2. *Theoretical.*

The vibrational energy term of anharmonic diatomic oscillator is given by

$$G\ (v) = w\ \ (v+\tfrac{1}{2}) - x\ w_e\ (v+\tfrac{1}{2})^2 + y_e w_e\ (v+\ \tfrac{1}{2})^3 + \ldots\ldots \quad (1)$$

where v = the vibrational quantum number;

w_e = the frequency (in cm^{-1}) of vibration about the equilibrium position;

x_e, y_e are constants which take into account the anharmonic nature of nuclear vibrations.

From (1) above we could derive

$$\triangle G = G\ (v+1) - G\ (v) = w\ - 2\ x\ w_e\ (v+1)\ \ldots\ldots \quad (2)$$

The rotational energy term of the molecule can be written as

$$F\ (v,\ J) = B_v\ J\ (J+1) + D_v\ J^2\ (J+1)^2$$
$$+\ [\text{terms in 3rd and 4th powers of } J\ (J+1)\ ]\ ;\ldots\ldots(3)$$

where B_v and D_v are coefficients whose values depend upon the vibrational quantum number, *i.e.*

$$B_v = B_o - \alpha\ (v+\tfrac{1}{2})\ + \ldots\ldots\ldots;$$

Alternately we could write

$$B_v = B_o - \alpha v + \ldots\ldots\ldots\ldots\ldots;$$

where B_o is the coefficient for the state of minimum vibrational energy and α is a small positive constant. The value of B_v depends upon the nuclear distance and the mass of the molecule, and is expressed as,

$$B_v = (h/8\pi^2).(1/I_v)$$

where I = moment of inertia = μr^2, μ being the reduced mass $(M_1M_2)/)M_1 + M_2)$;

r = Distance between the nuclei.

3. *Results.*

In the case of NO, O_2, Rydberg* has shown that for different electronic states,

$$(\triangle G)^2 = K.\ B^2_{v+1}$$

where K is a constant.

To verify the above relation in N_2, $(\triangle G)^2$ has been calculated from the results of vibrational analysis. This has been done for C $^3\pi$, B $^3\pi$, and A $^3\Sigma$ states. The results of rotational analysis give B_o from which B_v has been calculated for different vibrational levels. The

*Loc. cit.

various constants used have been taken from Jevon's Report*. The values determined have been tabulated in Tables I, II, and III.

TABLE I.

C $^3\pi$ state.

$(\Delta G)^2$	B^3_{v+1}
$3{\cdot}972 \times 10^6$	5·658
3·756	5·358
3·500	5·070
3·161	4·791

TABLE II.

B $^3\pi$ state.

$(\Delta G)^2$	B^3_{v+1}
$2{\cdot}903 \times 10^6$	4·322
2·815	4·141
2·712	3·967
2·618	3·797
2·522	3·630
2·430	3·470
2·341	3·314
2·250	3·163
2·164	3·017
2·076	2·875
1·991	2·738
1·910	2·604
1·830	2·476

*Jevon's Report on Band Spectra of Diatomic Molecules: Phys. Soc. 1932.

TABLE III.

A $^3\Sigma$ state.

$(\Delta G)^2$	B^3_{v+1}
$2{\cdot}050 \times 10^6$	2·869
1·974	2·790
1·896	2·714
1·820	2·638
1·745	2·565
1·672	2·492
1·600	2·421
1·530	2·351
1·464	2·283
1·392	2·216
1·327	2·151
1·250	2·087
1·181	2·024

In Fig. 1 are plotted the values of B^3_{v+1} against $(\Delta G)^2$ and the relation obtained is a straight line for each electronic state. It may be noted, however, that the slope of these lines is not the same for

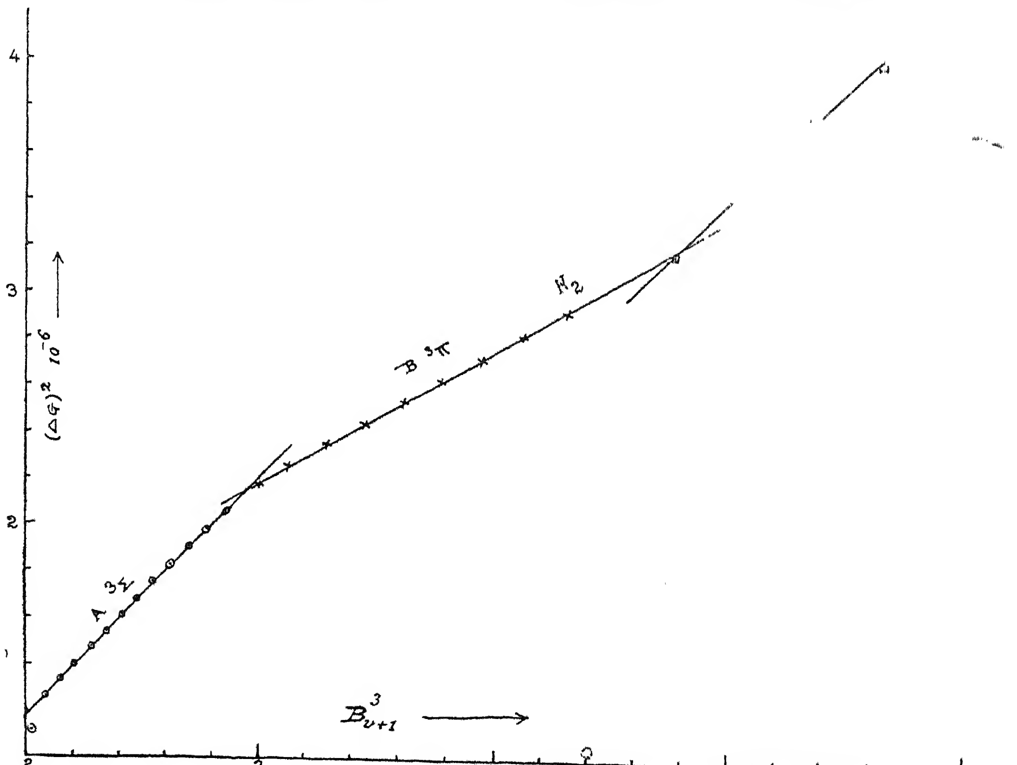

Fig. 1.

(Vide p. 1552 J. C. S. London)

all the electronic states examined and here the results are in disagreement with Rydberg's conclusions as far as this molecule is concerned. The graph for C $^3\pi$ state appears to be almost parallel to that of A $^3\Sigma$ state with an upward shift of $B^3_{v+1} = 0{\cdot}70$. It remains to be seen from the study of the behaviour of other molecules, how the constant K varies from one molecule to the other and whether, by its means, we could predict some unknown data in another electronic state.

Abstract.

The vibrational and rotational levels of nitrogen molecule in different electronic states are correlated and the results examined in the light of Rydberg's general conclusions on some other molecules.

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A NEW METHOD OF COUNTING DUST NUCLEI IN AIR

BY

G. R. PARANJPE AND Y. G. NAIK

While working on the problem of condensation of water-vapour on dust nuclei, it became possible to evolve a direct and rapid method of counting dust particles in air. This method appears to possess many advantages over the existing dust-counters.

Aitken's (1) dust-counter consists of a small expansion chamber with a piston arrangement for creating expansion. The air under investigation is admitted in this chamber after sufficient dilution. On creating an expansion, which is generally greater than 1·4 times the original volume, the water-vapour condenses on the dust nuclei and the drops enclosed between the two glass plates settle down on the bottom of a ruled plate. The number of drops, which is generally less than 10 per cc. is ascertained by observation through a microscope. The volume of air under actual investigation is about 1 cc.

The temperature of the chambers at which the drops are formed, rises very rapidly, and on account of the smallness of the chambers some drops evaporate before settling down. This leaves a possibility of some of the nuclei, that have been used up previously, coming up again in one or more subsequent expansions. Again it is possible according to Aitken (1) himself that some nuclei may be created by the friction of the piston, which is in direct connection with the expansion chamber and these might create drops in the succeeding expansions.

Nolan (2) remarks that no agreement has been reached by previous workers (3), while using the Aitken's dust-counter as to whether the showers brought down in the succeeding expansions should be counted or not. Again he says, "During the work carried out here, occasional observations were taken on the succeeding showers with the object of determining the error involved on the assumption that our method of counting the first shower is incorrect. It was found that the second shower was only of importance, its magnitude varying between 10% and 25% of the first shower".

It is again uncertain as to whether the drops formed at expansion ratios of about 1·4 and more do necessarily contain dust nuclei. According to C. T. R. Wilson (4) it is possible for drops to form on charged nuclei if the expansion ratio is greater than 1·4. On ac-

count of this uncertainty, Owen (5) has raised the same objection to this dust-counter.

A large number of observations have to be taken in order that the average count fairly represents the actual number. Since the count can conveniently record not more than 10 nuclei per cc., the air to be examined is diluted with dust-free air to 500 or even 1000 times the original volume. Thus the efficiency of the count is reduced.

In Owen's (5) dust-counter, the air under investigation is allowed to strike against a ruled glass plate, forcing it through a narrow slit with a known velocity. The nuclei stick to the glass plate and their number is counted by means of a high power microscope.

Experiments by Barus (6) showed a method of counting the number of particles per cc. by successive expansions. The size of the particles was determined by measuring the angular apertures of the corona rings. This process of estimating the number of particles by successive expansion appears to be uncertain inasmuch as he does not take into consideration the settling and evaporation of drops between two successive expansions. Moreover he does not take into consideration the experimental evidence quoted in this paper, *viz.*, that the size of the corona rings depends on the number of nuclei present in each experiment. Barus himself refers to the uncertain nature of his method, particularly so far as it concerns the number of particles in his experiments (Carnegie Institution publication—1906, No. 62, pp. 160-162). Two chambers based on the same principle give results for the number of particles which are very different from each other. The ratio of the two corresponding numbers is sometimes as large as 4 and the variation is not accounted for.

Owen (5, p. 23), however, found that all the nuclei do not stick to the glass plate at the first encounter. This was tested by Owen (5, p. 24) by allowing the same used up air to strike the glass plate once more, when some more nuclei were detected. It, therefore, remains uncertain as to whether all the available nuclei stick to the glass plate and get detected. Owen (5, p. 24) assumes that the ratio of the number of nuclei sticking to the glass plate and the total number is always constant and on this supposition he obtains the actual number of nuclei. The count seems to be nearly impossible if the nuclei are more than 200 per cc. in number. Dilution of air to a considerable amount will only be of avail in such a case, and it is well-known that the sample of air that is investigated upon very often contains thousands of nuclei per cc.

Owen (5, p. 27) has found the ultramicroscopic method to be unsatisfactory and unrepresentative on account of the extreme smallness of the actual volume coming under observation.

Whytlaw (7) observes, in his paper on the coagulation of smokes, that both the methods of counting dust nuclei (*viz.* Aitken's method and Owen's method) are unsuitable, the former (Aitken's) because the particles were so numerous in their system that much dilution would be necessary, and the latter (Owen's) because the ultramicroscopic particles would probably escape detection. In Whytlaw's method the particles are observed as in ultramicroscopic method, but only a small fraction of air has to be used every time for investigation and again about 50 observations are necessary in order that the final count represents the average value.

Most of the above difficulties have been surmounted in the method described in this paper. It is based on direct determination of the size and number of drops formed in a condensation on dust nuclei.

The size of the drops was determined by observing the angle subtended by the radius of the diffraction ring, seen through a cloud, when a parallel beam of monochromatic light passes through it. Angles were determined by means of a theodolite. The cloud chamber (flask) has a capacity of more than ten litres. A metal tank 4 to 5 times bigger than the flask is partially exhausted and sudden expansion is then caused in the flask by opening a large cock connecting them. Any desired expansion can be created in this way.

The radius of drops can be calculated from the formula

$$\text{Sin } \theta = (\text{N} + 0{\cdot}22)\ \lambda/2a.$$

where

a = the radius of the drops

θ = angle subtended by the radius of the corona

N = the order of the corona

λ = mean wave length of light used.

The quantity of water condensed in an expansion can be calculated according to C. T. R. Wilson method (4) and hence knowing the size of the drops, the number can be calculated.

The working expansion ratio was never more than 1·3, and thus the formation of drops without dust nuclei was impossible.

While working on the problem of condensation it was noted that both the size and the number of drops formed in a condensation was very largely influenced by the actual number of nuclei present in a sample of air, the condition of temperature and expansion ratio remaining the same.

In the literature on the subject of condensation no mention appears to have been made of the above fact. On the contrary different authorities have given results showing only the effect of the expansion ratio on the size of the condensed drops either at one or at different temperatures.

A series of experiments were made to see what variations in the size and the number of drops did actually take place by steadily increasing the number of nuclei in the chamber and forming a condensation under identical conditions. As the nuclei go on increasing the size of the drops goes on diminishing and the number of drops consequently increases. The following sets of results show the variation in the size of drops for different sets. The expansion ratio is constant for each set as also the quantity of water condensed in consequence.

Expansion ratio	Quantity of water condensed x 10^{-6} grms. per cc.	Nuclei increasing.	Radius of drops in μ	No. of drops formed per cc.
1·074	1·825	↓	16·08	106
			10·63	364
			6·81	1382
			5·87	2151
			5·35	2855
			4·90	3700
1·106	2·520	↓	16·90	129
			14·61	193
			12·31	400
			7·37	1525
			6·06	2707
			5·63	3363
			5·23	4318
1·140	3·171	↓	15·15	218
			8·12	1418
			6·69	2530
			6·40	2897
			5·88	3736

Expansion ratio	Quantity of water condensed x 10^{-6}grams. per cc.	Nuclei increasing.	Radius of drops in μ	No. of drops formed per cc.
1·176	3·689	↓	16·08	212
			9·71	963
			7·21	2350
			6·90	2696
			6·55	3138
			5·13	6433
1·215	4·368	↓	18·99	152
			11·79	641
			8·37	1778
			7·37	2605
			7·18	2822
			5·34	6847
			4·76	9685

Previous workers on the subject assumed that the size of the drops depended only on the expansion ratio and temperature. The results quoted above indicate that such an assumption is impossible. Drops of various sizes from 4 to 18 μ can be formed by varying only the number of nuclei. The last column in the above sets gives the number of drops formed in consequence of an expansion. It is therefore evident that the increase in the number of nuclei increases the number of drops. This result suggests the possibility of counting the number of nuclei. The correct estimation of the number of nuclei by this method depends upon the following assumptions :—

(1) All the available nuclei are used up in the formation of the cloud so that no nuclei remain unused.

(2) There is no loss in the number of nuclei by fusion of drops, *i.e.*, there is no possibility of coagulation under the conditions of the experiments ; in other words, the number of drops is equal to the number of nuclei.

(3) There is no possibility of drops being formed without any dust nuclei whatever.

It has been shown below that all the assumptions are justified.

(1) A certain number of nuclei was inserted in the dust free flask. An expansion was made and the number of drops formed in consequence was calculated. The cloud was next allowed to settle completely. Without bringing the flask to its initial atmospheric pressure, further expansion was made. (This particular method was adopted because it was found that thick cotton filter and water trap were usually insufficient to keep off the entry of fresh nuclei from the air directly entering the flask.). Thus any nuclei which might have been left over by the first expansion could be utilised in forming drops in the successive expansions.

If the number of nuclei originally inserted in the condensation chamber is exceedingly large then there is a possibility of a few nuclei remaining over ; but their number is always a very small fraction of the original. Such extreme cases are, however, not contemplated in this paper. A careful investigation has shown that if the initial number of nuclei for the first cloud is less than about 3000 per cc. in the flask, it is impossible to form a second cloud. If the initial number is greater than about 3000 per cc., a few nuclei are found to remain over to form a second cloud in the successive expansion. The number of nuclei left over in such a case is usually so small that it does not amount to more than 2 or 3% of the original number. For a large number of nuclei of about 6600 per cc. the nuclei left over were nearly 150 per cc. which were enough to yield the second cloud. There can be two reasons for these left over nuclei. Either, they were not used up at all in the first expansion or they were used up in the formation of drops but soon recovered their original nuclear state due to evaporation. The latter reason seems to be more probable. In any case these left over nuclei are sufficiently small in number to be neglected even if they remain unused in the first expansion.

(2) The corona ring attained a fixed and well defined size in only a fraction of a second and remained unaltered till the cloud settled down. This fact excluded the possibility of fusion of nuclei and drops of abnormal sizes.

(3) C. T. R. Wilson (4) has stated that for expansion ratios less than 1·3, dust nuclei are absolutely necessary for the formation of drops. It was observed that no drops are formed in the dust-free flask at the working expansion ratios, which are uniformly below 1·3.

The experimental flask in the present work was of about 10 litres capacity. A volume of 1000 to 2000 cc. of air to be examined could be inserted at will in the flask. Thus the result can be more representative.

There was no dust counter available and so a comparison of the different methods was not possible. The actual method proposed in this paper is given below.

If E be the expansion ratio at which air to be examined is inserted into the dust-free flask, $(E-1)/E$ is the actual volume of dust bearing air per cc. in the flask. If now N_1 be the number of nuclei per cc. in the flask at an expansion ratio E_1, N_1E_1 is the number of nuclei per cc. before the expansion is made. Each cc. of air in the flask represents $(E-1)/E$ cc. of air inserted from outside. Therefore the number of nuclei (N) per cc. in the specimen of air is equal to $N_1E_1E/(E-1)$. N must come out to be the same whatever may be the value of N_1, E_1 and E. A number of observations were made to verify the accuracy of the count for a given specimen of air by varying E_1 and E.

Each set of results given below was taken for a different specimen of air containing different number of nuclei. It can be seen from the table that the values of N do not differ much and involve an error always less than 10% by taking an average.

	E	E_1	N_1	N	Deviation from mean.
(a)	1·174	1·134	578	3420	
	1·276	1·142	942	3900	7%
	1·276	1·205	811	3300	
(b)	1·174	1·139	3280	22170	8%
	1·284	1·142	5600	25350	
(c)	1·156	1·114	381	2820	6%
	1·298	1·114	653	3170	
(d)	1·157	1·115	2140	17570	
	1·277	1·112	3420	17510	
	1·277	1·199	2810	15500	7%
	1·286	1·115	3290	16490	
(e)	1·163	1·125	1480	11900	1%
	1·284	1·125	2340	11850	
(f)	1·233	1·108	1060	6210	6%
	1·233	1·190	1060	6700	

The reliability of the method suggested here has been checked as mentioned above by actually making measurements on different amounts of dust bearing air from the same specimen. It is clearly seen from the above table that while E_1, E and N_1 have different values, the value of N remains nearly the same for each sample.

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POLLUTION OF BOMBAY AIR BY SMOKE

BY

Y. G. NAIK

The investigation was undertaken on behalf of the Smoke Nuisances Commission, Bombay. A series of observations lasting for seven days were made at four different localities situated in the mill area. At each centre two observations, *viz.*, one in the morning and one in the evening, were taken.

The method described in the preceding paper was employed in estimating the number of smoke particles. Air samples were brought in specially designed flasks and were then investigated in the cloud chamber for the estimation of the number of smoke particles.

The results of the present investigations are given below:—

MORNING OBSERVATIONS

Date.	Time	Byculla Bridge.	Lalbaug.	Fergusson Road.	Sewri.
March 29th...	7-8	1760	1990	2130	2490
,, 30th...	6-7	2130	1460	2420	2910
,, 31st...	6-7	2650	2640	3290	5030
April 1st ...	7-8	1860	2920	4240	1500
,, 2nd ...	8-9	1400	1060	1500	880
,, 3rd ...	8-9	1450	1510	2140	3550
,, 4th ...	7-8	2270	2860	4090	4260
Average ...	...	1930	2060	2830	2940

EVENING OBSERVATIONS

Date.	Time	Byculla Bridge.	Lalbaug.	Fergusson Road.	Sewri.
March 29th...	7-8	3540	3490	3750	2920
,, 30th...	8-9	3290	2760	3680	4090
,, 31st...	10-11	3360	2640	4660	2060
April 1st ...	7-8	1990	3300	2990	1490
,, 2nd ...	9-10	3100	2730	3410	1990
,, 3rd ...	7-8	2420	7050	8630	3980
,, 4th ...	7-8	3230	3040	4500	2920
Average ...	...	2990	3570	3950	2780

The number under each head represents the number of smoke particles per cubic centimetre.

From the results it is evident that the number of smoke particles varies between 2000 to 4000 per cc.

The samples of air from Band Stand and Pherojshah Mehta Gardens did not give rise to any cloud (forming a corona) in the observation flask, indicating thereby that the number of particles must be less than 100 per cc. which is the least number that can be measured with accuracy in the present case.

The relative variation in the number of particles is clearly seen in the graphs.

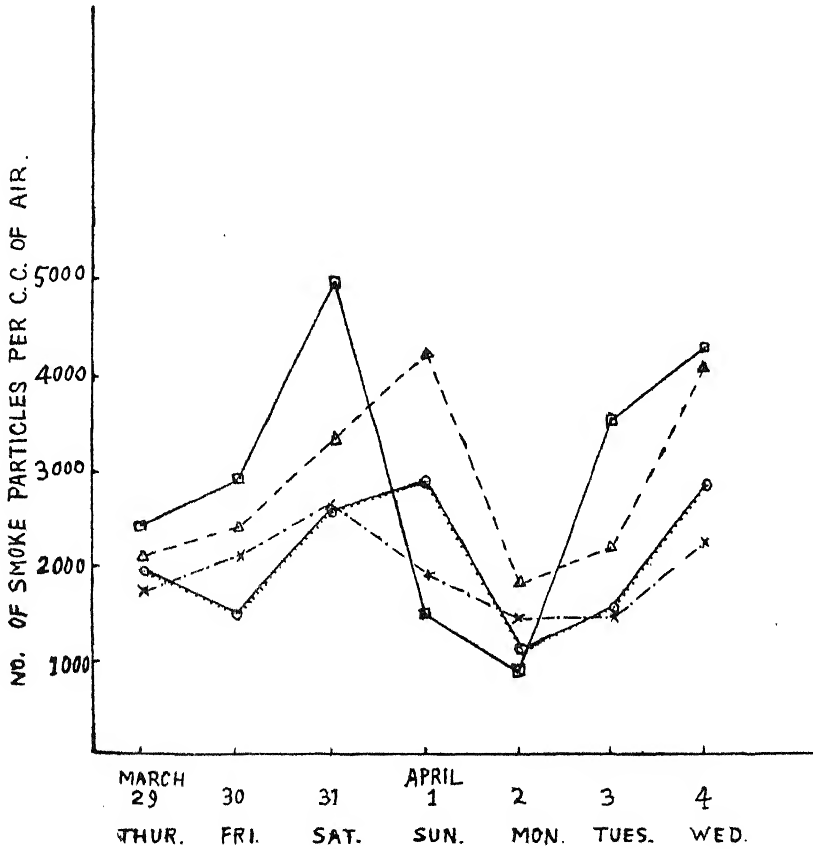

Fig. 1.

Morning Results.

The Morning graphs for Sewri show a remarkable phenomenon :-
(*i*) The evening pollution is less but the morning pollution on week days except Sundays and Mondays is considerably higher than at

other places. (*ii*) On Monday, however, the morning pollution is the least of all. Both these facts can be explained if we suppose that during night, the wind carrying smoke from Parel locality drifts towards the East and causes a greater pollution towards that side. The sudden decrease in pollution on Monday may be traced to the fact that on Sunday the mills remain closed and that there is practically no traffic in that area.

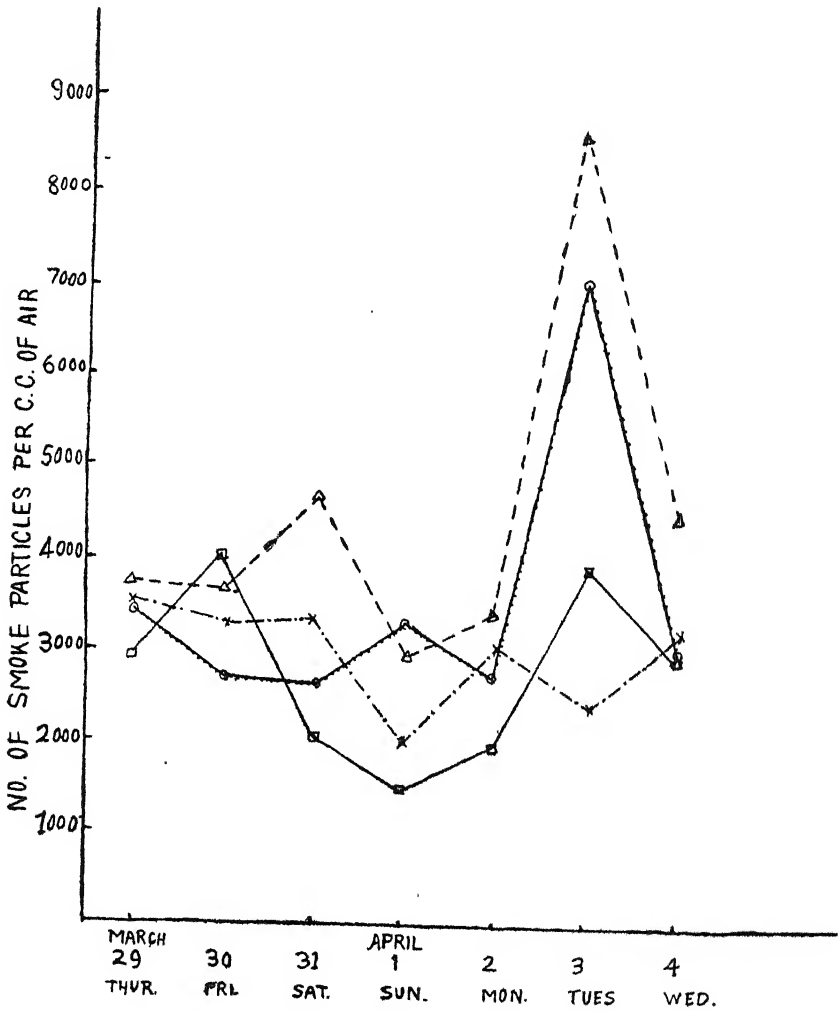

Fig. 2.

Evening Results.

△ - - - - - Fergusson Road. ○ —·—·— Lalbaug.
× —·—·— Byculla. □ ———— Sewri.

From the Evening graphs, it is quite evident that : (1) The Fergusson Road locality is more affected by smoke than any other. The smoke pollution can, on average, be taken in the following increasing order :—

(1) SEWRI, (II) BYCULLA, (III) LALBAUG, (IV) FERGUSSON ROAD.

(*ii*) The number of smoke particles in general varies at all these places between 2000 to 4000 particles per cubic centimetre of air. On the 3rd April, however, there is a sudden increase to be observed in Lalbaug and Fergusson Road area. Sewri shows the least pollution on an average.

Part of the pollution at Byculla and Lalbaug may be attributed to the heavy volume of traffic whereas the pollution at Fergusson Road may be principally due to the smoke discharged by the mills.

Thanks are due to the authorities of the Royal Institute of Science for giving the necessary permission to conduct this investigation and to the Smoke Nuisances Commission for granting permission to publish the results.

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Bombay.

MOUNTING CONCAVE GRATINGS OF SMALL RADIUS OF CURVATURE

BY

H. N. DESAI

Many laboratories have small replica concave gratings of radius of curvature of about a metre. Such gratings can be used for demonstrative purposes as also for carrying out preliminary work in spectroscopy, if they are suitably mounted. For such replicas the well-known Rowland mount or the Eagle mount (E. C. C. Baly's Spectroscopy, Vol. I, Chapter 7) is rather complicated and costly and they are not so easy to erect in small laboratories as the comparatively simple Paschen-Runge type.

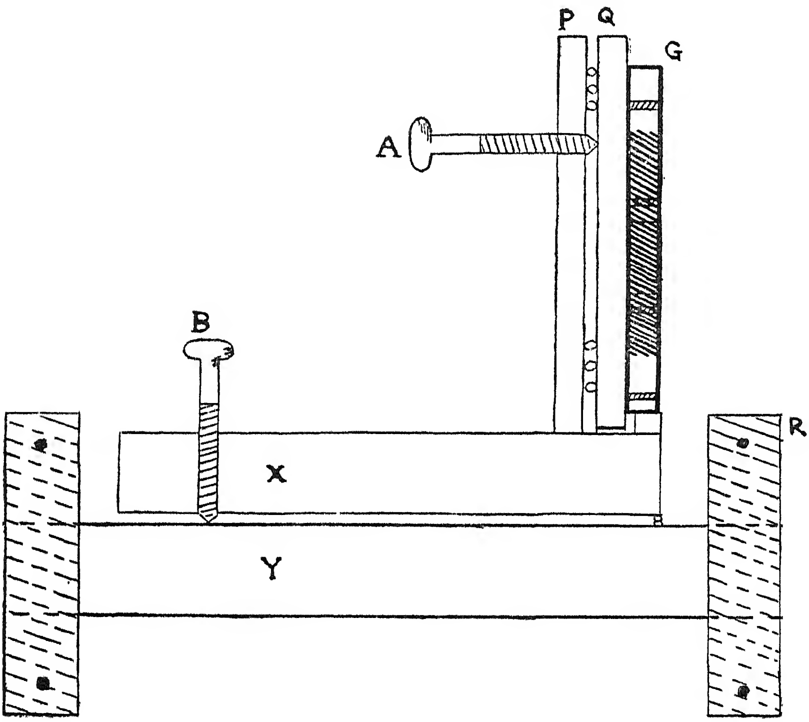
The following gives a description and details of focusing arrangements for a grating of radius of curvature R = 848 mms. mounted on the Paschen-Runge type in our laboratory. The replica can be mounted with the help of a carpenter at a small cost of about Rs. 30.

One advantage of this type of mount is that it does not require a dark room as everything is fitted up in a small light-tight box; precaution has to be taken only at the time of charging the film. This can be easily done by fixing a black curtain in the front portion of the box. Moreover, this does not require focusing every time, as the focusing adjustments are done once for all in the beginning. The entire spectral region or any portion can be photographed without disturbing any other arrangement simply by putting the films at the required place.

A detailed description of the mounting and focusing arrangement is given with a hope that it may prove useful to other laboratories.

The grating used in this particular case is a Wallace's replica of Rowland grating (prepared by the Central Scientific Company, Chicago) of radius of curvature R = 848 mms. and has 15260 lines to the inch.

Grating Holder :—The grating G is mounted on a holder as shown in Fig. 1 and the holder is fixed on the base board (described later) by means of rubber bands R,R.



GRATING HOLDER (SIDE VIEW)

FIG. 1

The grating is fixed on the plate Q by rubber bands, and can be given an angular turn about the vertical axis by means of screw A which passes through the middle of P, the end of P and the middle of Q being hinged together. The plate P is fixed on a horizontal wooden plate X, which itself is hinged to the plate Y. The plate Y is finally fixed to the base board by rubber bands R,R. The screw B permits the movement of the grating about the horizontal axis. Another screw not shown in the figure is fixed in plate Y for tilting the whole system about another horizontal axis perpendicular to the previous one.

Film Holder :—The film holder is made from two rectangular wooden plates fixed by means of bolts and nuts as shown in Fig. 2.

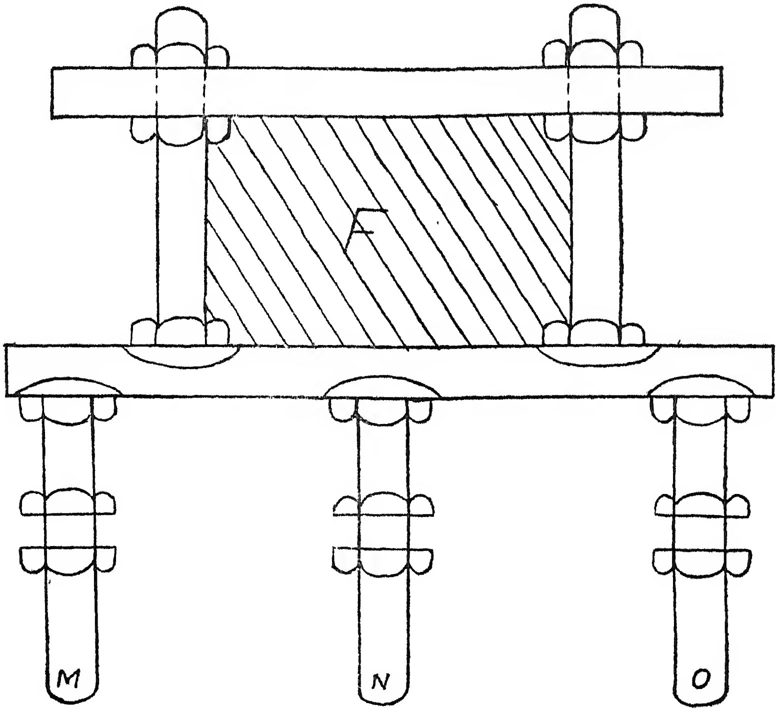
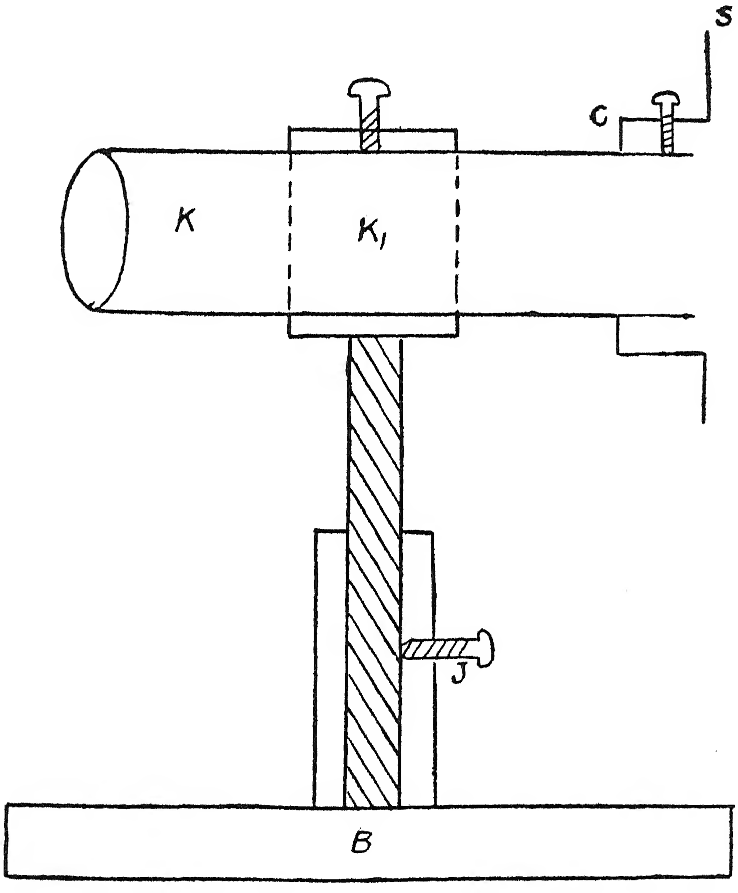


PLATE HOLDER (Front View)

Fig. 2

On both the plates identical arcs of diameter R are made and on each plate the portion not enclosed within the arc is made about 5 mms. thinner than the rest to allow rubber bands 5 mms. wide to be fixed along the arc. The film is pressed on the arcs at the base and the top by rubber bands. The width of the film F, *i.e.*, the distance between the two wooden plates can be varied by shifting the nuts at the top of the bolts. The film thus takes up the curved shape of an arc of diameter R. The upper plate can be shifted backwards or forwards or slightly sideways by cutting suitable grooves through which the two bolts pass. The film holder is fixed by nuts to the base board by cutting three grooves in the board for the three bolts M, N and O. Shifting the nuts along the bolts, the plate holder can be raised or lowered with respect to the base board. The grooves allow backward and forward motion of the holder as a whole, as also the rotation about the middle bolt N which forms a vertical axis passing through the arc on which the film rests.

The Slit :—Two safety-razor blades serve as jaws of the slit and are fixed by means of screws passing through slots to a thin brass plate S which has a rectangular slot in the middle (Fig. 3). S itself is soldered to a collar C which fits on a long hollow tube K and is fixed by a screw. The tube K slides horizontally in a short tube K_1 which is fixed on a rod sliding up and down in a hollow tube fixed on a wooden base B.



SLIT (Side View)

Fig. 3.

The base B slides backwards and forwards in grooves of a frame fixed on the base board (may even be directly fixed on the board).

The light-tight box is prepared with sides such as can be opened whenever required. The inside of the box is painted black with black Japan. As the spectral region from about $\lambda = 1850$ to $\lambda = 10600$ in the first order would be sufficient for our purpose, the base board of our mounting is made smaller than that required for the whole Rowland Circle. The dimensions are given, in Fig 4. The length of the arc of the film holder is 46 cms. and the $\angle NGS$ about $22°30'$.

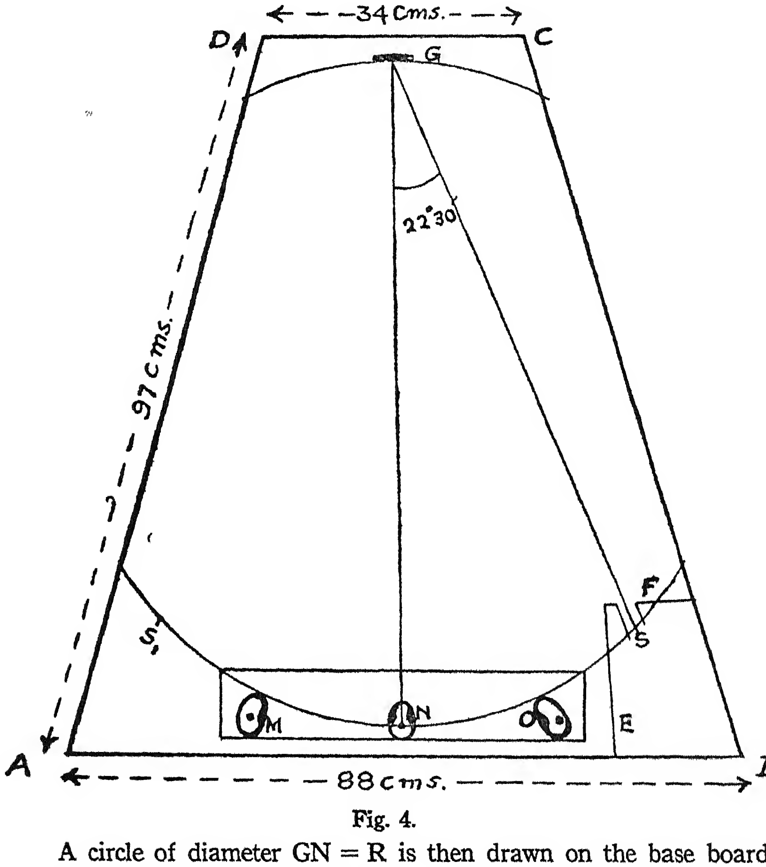


Fig. 4.

A circle of diameter $GN = R$ is then drawn on the base board and the following adjustments made. The grating is placed so that the centre of its surface is vertically above the point G on the curve (Fig. 4), and the bolt N of the film holder is kept at the point N. GS is drawn inclined to GN at an angle of $22°30'$ which we have chosen for our purpose. The bolts of the film holder are fixed in grooves M, N and O. The slit is kept at S and is separated from the main part of the box containing the grating by a wooden partition E and thick black curtain F fixed on the sides and allowing

the tube K (Fig. 3) to pass through. The curtain fits tightly round K by means of elastic bands.

Focussing :—First the central parts of the grating, slit and plate holder are brought in the same plane by adjusting the heights of the last two. Thereafter the whole curve of the film holder is brought to its proper position in the following way. In the film holder, place a card board strip (instead of the film) with a number of equidistant slits cut on it as shown in Fig. 5 ; keep the central slit O at N as in Fig. 4 and close all the other slits.

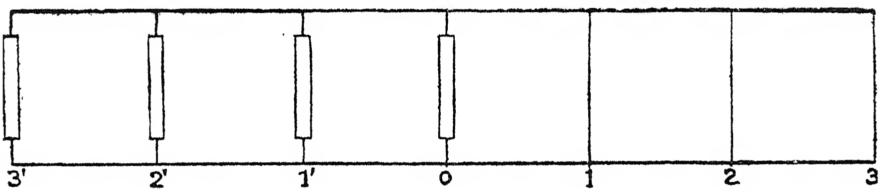


FIG. 5

Place the source of light (an electrical lamp) in front of O and adjust the grating by screws A and B (Fig. 1) till the image of the slit falls on the slit itself. Shift the film holder as a whole backwards and forwards through the slot at N till the image is sharpest. Closing the middle slit, open slit 1. Similarly try the other slits 2 and 3 adjusting as before. Small scales marked near the grooves at M and N will be helpful. The whole process ensures that the film forms an arc of the Rowland Circle and that the grating is tangential to it. Loosening the upper nut, the upper plate of the film holder has to be moved in the grooves till the images obtained as above are sharp all along their vertical lengths.

Having thus adjusted the grating and the film holder the image of the source, duly collimated, is focussed on the slit by means of a lens and the slit brought on the curve at S (Fig. 4) by moving it backwards and forwards till a sharp image of the slit is obtained at S_1. The width of the slit is adjusted as usual till the intensity of the spectral lines is maximum without further reducing the width of the lines.

In this condition if the source (a sodium burner or an arc between impure carbon poles) is kept in front of the slit S (Fig. 4), the line spectrum can be observed on a ground surface (an unexposed developed film would do well). The slit is moved backwards and forwards, the fine adjustment being made by moving the tube K in K_1 till the lines are seen sharpest. The lines are somewhat lozenge-shaped or diffused in the middle at first and can be made sharp by

giving the slit a slight rotatory motion about a horizontal axis so as to make the slit parallel to the grating rulings. For noting the best position, a pointer is attached to S (Fig. 3) and a scale is kept on K in front of it. Then the whole adjustment of the apparatus is complete.

With the dimensions chosen, the spectrum is normal at $\lambda = 6370$ A°U. The film holder covers the region from $\lambda = 1887$ to $\lambda = 10553$ in the first order and there is an average dispersion of 19·5 A°U per mm. along the arc. A portion of the spectrum observed with an A. C. carbon arc with $SrCl_2$ on the lower pole is reproduced below.

For measuring the wave-lengths, known lines in the spectrum itself may be used or alternately an arrangement workable from outside the box can be made to cover the lower half of the film after the exposure and then a known spectrum superposed on the upper half of the same film.

I wish to thank Dr. J. S. Badami for suggesting this work and for his continued interest in the same.

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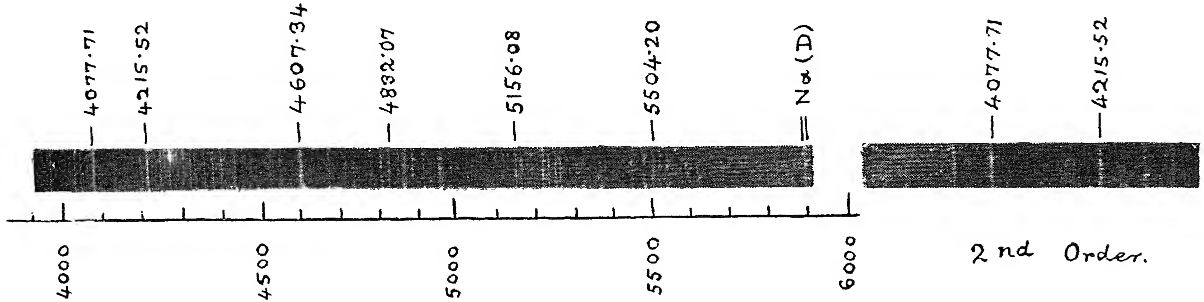
PLATE I



ARC SPECTRUM OF STRONTIUM

AN OPTICAL METHOD OF MEASURING POISSONS RATIO OF THIN GLASS PLATES

BY

V. D. MAJUMDAR

When a thin rectangular glass plate is clamped at the edges it gets deformed into a surface that very much resembles a saddle. When an optically plane glass plate is placed over this surface, a hyperbolic pattern of Newtons fringes is seen. A measurement carried on geometric disposition of the assymptotes supplies the necessary material for the calculation of σ, the Poissons ratio for the glass plate. Straubel (Cl. Schafer. Mechanic I. p. 540 122.) has proved that if the angle between the assymptotes of the hyperbola be α then

$$\sigma = \tan^2(\alpha/2).$$

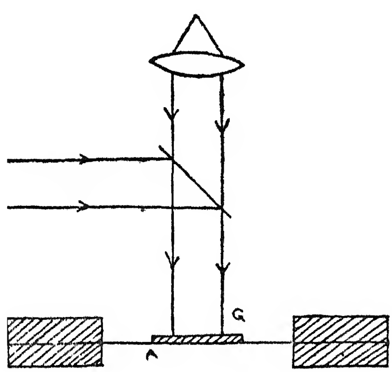


Fig. 1.

The glass plate A under observation was placed on two glass slabs. Over each edge of the plate a second glass block was placed. The plate thus clamped at the edges was deformed. Over the glass plate another glass plate G of about a mm. in thickness was placed. By a suitable optical arrangement a beam of parallel monochromatic light was thrown on the plate G. The Newtons fringes formed between the plates A and G were then observed by a microscope from above.

A series of bright and dark conjugate hyperbolas were seen. If the major and the minor axes of the hyperbola be a and b then the semi-angle $\alpha/2$ between the assymptotes is such that

$$\tan \alpha/2 = b/a = \sqrt{\sigma}$$
$$i.e.\ \tan^2 \alpha/2 = b^2/a^2 = \sigma$$

The following table shows that the above mentioned angle between the assymptotes remains constant, and the lengths of the axes of the innermost system of fringes depends upon the magnitude of the deformation.

TABLE I.

Thickness of the glass plate = ·133 cms.

Deformation.	a Divisions.	b Divisions.	$\frac{b}{a}$	$\frac{b^2}{a^2}=\sigma$
1. 1st Bright fringe...	604	245	·568	·323
2nd ,, ,, ...	710	343	·568	·323
2. 1st ,, ,, ...	831	470	·565	·319
2nd ,, ,, ...	958	532	·565	·319
3. 1st ,, ,, ...	579	330	·570	·325
2nd ,, ,, ...	735	418	·570	·325
4. 1st ,, ,, ...	749	420	·560	·313
2nd ,, ,, ...	917	514	·560	·313
5. 1st ,, ,, ...	1061	596	·562	·316
2nd ,, ,, ...	1207	678	·562	·316
6. 1st ,, ,, ...	517	295	·570	·325
2nd ,, ,, ...	585	333	·570	·325

This represents a typical measurement on two different fringes in the same system, *i.e.*, the same deformation. Experiments were carried on for different deformations in order to test the theory that the angle between the assymptotes is independent of the magnitude of the deformation.

In the following case the plate was laid upon the stage of the microscope and held down by two flat weights at the two ends,

TABLE II.

Thickness of the plate : 0·0148 cms.

Deformation.	a Divisions.	b Divisions	$\frac{b}{a}$	$\frac{b^2}{a^2}=\sigma$
(1)	1650	924	0·560	0·313
(2)	1501	847	0·564	0·318
(3)	1882	1054	0·560	0·313
(4)	1523	856	0·562	0·316
(5)	1231	685	0·556	0·309

The number of fringes in a given interval was a sufficient evidence to assume that the deformation was a different one at each time.

The value of σ thus measured agrees well with that obtained by standard laboratory methods.

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CONDENSATION OF PHENOLS AND PHENOLIC ETHERS WITH ACETONE-DICARBOXYLIC ACID SYNTHESIS OF ββ-SUBSTITUTED GLUTARIC ACIDS

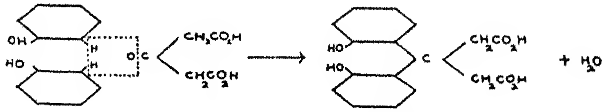
BY

V. M. DIXIT AND G. N. GOKHALE

Acetone-dicarboxylic acid has been condensed with phenols in the presence of various catalysers, the commonest amongst which is conc. sulphuric acid. [See :—*Coumarin-acetic acids,* by Fries and Volk (Annalen, 1911, *379,* 90), Dey (Trans. Chem. Soc. 1915, *107,* 1606), Dey and Row (J. Ind. Chem. Soc. 1924, *I,* 110) and Limaye (J. Ind. Chem. Soc. 1927 *IV,* 159). *β—Substituted glutaconic acids* by Limaye and Dixit (vide Proc. Ind. Sc. Congress 1930, 167). Limaye and Bhave (J. Ind. Chem. Soc. 1931, *VIII,* 137) and Dixit (J. Ind. Chem. Soc. 1931, *VIII,* 787). The acetone-dicarboxylic acid acts in the enolic form in these reactions.

A new acidic compound was prepared by condensing phenol (2 mols.) with acetone-dicarboxylic acid (1 mol.) in the presence of dilute sulphuric acid (75 p.c.). It was a crystalline dibasic acid (Formula :—$C_{17}H_{16}O_6$; Eq. Wt., 158 and m.p. 234° (decomp) which formed insoluble copper and lead salts. Aqueous solution of the acid gave a bluish green coloration with ferric chloride. Similar new acids were also obtained from o-cresol, quinol and p-cresylmethyl ether. Phenol gave the greatest yield.

The constitution of ββ-2 : 2′-dihydroxy-diphenyl-glutaric acid is proposed for the new compound from phenol. The condensation is assumed to take place as follows :—



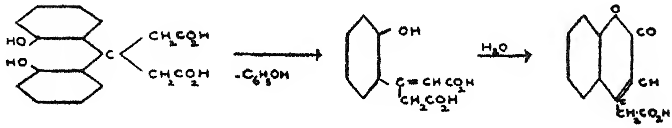
ββ-2 : 2′-Dihydroxy-diphenyl-glutaric acid.

The acetone-dicarboxylic acid acts in the ketonic form. The results of the following reactions bear out the given constitution :—

(1) *Action of conc.-sulphuric acid at 50°-60°.*

The compound breaks up almost quantitatively into coumarin-4-acetic acid, identical with that prepared by Limaye (loc. cit.) and

phenol, identified by its tribromo-derivative. The reaction is explained as :—



The intermediate glutaconic acid cannot be isolated [Dey. (loc. cit.)] except in the decomposition of the corresponding glutaric acid obtained from p-cresyl-methyl ether.

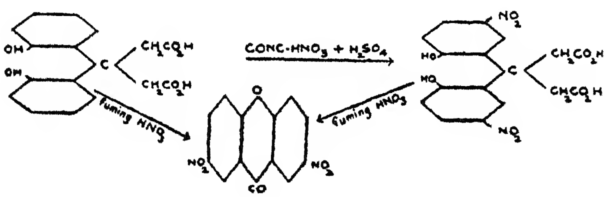
(2) *Oxidation.*

The compound when oxidised by either alkaline permanganate or chromic acid gave 4-methyl-coumarin and phenol.

(3) *Action of nitric acid.*

On treating the new substance with conc. HNO_3 in the presence of a small quantity of H_2SO_4 in cold, a dinitro derivative was obtained.

Heating this dinitro derivative or the original glutaric acid, with fuming nitric acid in sealed tubes gave much of $\beta\beta'$-dinitro-xanthone and a small quantity of picric acid. The reaction can be represented as :—



(4) *Action of KOH.*

Fusion of the glutaric acid with moist caustic potash at 180°C gave 2 : 2′-dihydroxy-benzo-phenone, identical with that obtained by Richter [J. Pr. Chem. year 1883, (2), *28*, 285].

(5) *Knoevenagel Condensation.*

Unlike the esters of coumarin-4-acetic acids, the ester of the new acid or the acid itself did not yield any condensation product with salycilic aldehyde in spite of several attempts.

(6) *Synthetical Reactions.*

The dimethyl ester of the new glutaric acid formed the corresponding apo-camphoric ester by condensing with dimethyl oxalate

according to the method of Komppa (Trans. Chem. Soc. 1911, *99*, 2020) and it also condensed with dimethyl phthalate according to the method of Dieckmann (Ber. 1899, *32*, 2227).

Besides these, the new glutaric acid formed a number of characteristic derivatives, which are described in the table attached further. The corresponding glutaric acids obtained by condensing acetone-dicarboxylic acid with *o*-cresol, quinol and p-cresyl-methyl ether respectively showed analogous equivalent weights, analytical data, salts and behaviour with conc. sulphuric acid.

In converting the $\beta\beta$-2 : 2′-methoxy-4 : 4′ methyl-phenyl-glutaric acid which is obtained from p-cresyl-methyl ether, into the corresponding 6-methyl coumarin-4-acetic acid by sulphuric acid, the intermediate (β-2-methoxy-5 methyl-phenyl glutaconic acid) was isolated. This on keeping in conc. sulphuric acid changed to the 6-methyl coumarin-4-acetic acid.

EXPERIMENTAL

(1) $\beta\beta'$-2 : 2′-*Dihydroxy-diphenyl-glutaric acid.*

Pure powdered citric acid (25 g.) was heated with conc. sulphuric acid (75 g.) at 60°-70° for about half an hour. The mixture was cooled and ice (12 g.) was added to it, keeping the temperature below 5°C. Freshly distilled phenol (20 g.) was added with shaking and the reaction mixture kept for 24 hours at the room temperature. It was then poured over ice (100 g.). The white precipitate which came out after 3-4 hours was separated by filtration, washed and boiled with water and filtered again. The insoluble matter on the filter contained coumarin-4-acetic acid (m.p. 172° decomp. Eq. wt. 204). The filtrate was boiled with neutralised animal charcoal, filtered and concentrated. The glutaric acid which separated was further crystallised from hot water. Colourless prismatic crystals, m.p. 234° (decomp) ; yield 50 p.c. with respect to phenol. (Found :- Eq. wt. 158·6 ; C, 64·33 ; H, 4·99. $C_{17}H_{16}O_6$ requires Eq. Wt. 158 ; C, 64·55 and H, 5·06 per cent).

Soluble in hot water, alcohol, acetone, acetic acid ; sparingly soluble in ether, benzene, chloroform and petroleum. Gives bluish green coloration with $FeCl_3$. Dissolves in $NaH\text{-}CO_3$ with effervescence and yellowish coloration.

The same glutaric acid was obtained by condensing free acetone dicarboxylic acid (14·6 g.) with phenol (20 g.) in sulphuric acid (50 cc. of 75 p.c.). Prismatic crystals m.p. 234° decomp.) ; Yield, 30 p.c.

Lead Salt : Lead acetate solution was added to the solution of the glutaric acid in excess of KOH. The precipitate was separated by filtration, washed with KOH, water and alcohol respectively and crystallised from boiling water. Small prisms, (Found.—Pb, 39·66 ; $C_{17}H_{14}O_6Pb$, requires Pb, 39·74 per cent.).

Copper Salt : This was obtained by adding a solution of copper acetate to a neutral solution of the potassium glutarate. Green prismatic plates from hot water ; yield, almost quantitative. Contains 2 mols. of water of crystallisation. (Found.-Cu, 15·43 ; $C_{17}H_{14}O_6Cu$, $2H_2O$ requires Cu, 15·25 per cent.).

(2) *Action of Conc. Sulphuric Acid.*

(*a*) *Coumarin-4-acetic-acid* :—A solution of pure $\beta\beta'$-2 : 2'-dihydroxy-diphenyl-glutaric acid (5 g.) in conc. sulphuric acid (60 cc.) was kept overnight and then warmed in a water bath at 50°-60° for about 8 hours. It was cooled and poured over ice (120 g.). The white precipitate was separated by filtration, washed with water and hydrochloric acid, and then crystallised from alcohol. Small needles, m.p. 186° (decomp) ; yield, 1·5 gms. (Found.—Eq. wt. 203·5 ; C, 64·59 ; H, 3·98. $C_{11}H_8O_4$ requires Eq. Wt, 204 ; C, 64·71. H, 3·92 per cent.). Identified with the synthetical Coumarin-4-acetic acid of Limaye (loc. cit.). On heating at its m.pt. it gave 4-methyl-coumarin ; m.p. 80° mixed with known 4-methyl-coumarin, m.p. 78°.

(*b*) *Phenol :* The filtrate obtained in (*a*) was neutralised by passing ammonia through it and the phenol was precipitated as tri-bromo-phenol by saturation of the solution with bromine. Needles from alcohol, m.p. 82°, Yield 1·2 gms. Mixed with tribromo-phenol, m.p. 81°.

(3) *Oxidation.*

$\beta\beta'$-2 : 2'-Dihydroxy-diphenyl-glutaric acid (5 g.) was heated with alkaline potassium permanganate solution (100 cc. of 3%) for three hours on a boiling water bath and the mixture was filtered. The filtrate when concentrated and acidified, gave coumarin-4-acetic-acid ; long needles from dilute alcohol, m.p. 172° (decomp) ; Yield, 0·6 gms. The residue on the filter, when dissolved in dilute HCl and extracted with ether gave a small amount of 4-methyl coumarin m.p. 80°.

(4) *Action of concentrated HNO_3.*

(*a*) *$\beta\beta'$-2 : 2'-Dihydroxy,-5 : 5'-dinitro-diphenyl-glutaric acid* :—

$\beta\beta'$-2 : 2'-Dihydroxy-diphenyl-glutaric acid (2 g.) was dissolved in sulphuric acid (20 gms. of 20%) and conc. HNO_3 (15 cc. of sp. Gr. 1·4) was added to it gradually in cold. The yellow crystalline solid which separated from this after two days, was filtered, washed

and crystallised, from hot water. Prismatic plates, m.p. 204° (decomp) ; Yield, 25 p.c. (Found : Eq. wt. 204·5 ; N, 6·75 ; $C_{17}H_{10}O_{10}N_2$ requires Eq. wt. 203 ; N, 6·89 per cent.).

(*b*) *ββ'-Dinitro-xanthone :*

ββ'-2 : 2'-Dihydroxy-diphenyl-glutaric acid (2 g.) was heated with fuming nitric acid, (1·5 cc. contained in a small tube) in a sealed carius tube from 80°—240° for about 48 hours. The contents were filtered, and the residue on the filter washed with sodium carbonate solution followed by small quantities of water. Yellow needles from alcohol, m.p. 260° ; yield, 20 p.c. Mixed with ββ-dinitro-xanthone prepared from xanthone by the method of Perkin (Trans. Chem. Soc. 1883, *52*, 187) m.p. 261°. The same nitro-xanthone was produced on treating the ββ'-(2 : 2'-dihydroxy-5 : 5'-dinitro-diphenyl)-glutaric acid with fuming nitric acid as above. Yellow needles, m.p. 261° ; yield, 30 p.c.

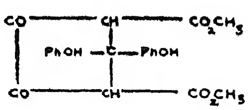
Picric acid (m.p. 122°) was formed by heating either the original glutaric acid, dinitro glutaric acid in (*a*), or the dinitro-xanthone (*b*), with conc. HNO_3 for about 2-3 hours.

(5) *Action of KOH.*

2 : 2'-Dihydroxy-benzophenone :

ββ'-(2 : 2'-dihydroxy-diphenyl)-glutaric acid (2 g.) was mixed with solid caustic potash [(3 g.) moistened with water] and the mixture heated in a suitable retort in an oil bath at 180°. The residue in the retort was diluted in cold and was immediately acidified with HCl at a low temperature. The solid which separated was filtered, washed and crystallised from petroleum ether. Yellowish prismatic crystals, m.p. 59°-60° ; yield, 20 p.c. Reddish brown coloration with Ferric chloride. Mixed with 2 : 2'-dihydroxy-benzophenone of Richter (loc. cit.) m.pt. 59°. On boiling this compound with sulphuric acid and pouring the solution in water, xanthone was obtained ; yellowish needles from alcohol, m.p. 174°C.

(6) *The condensation with dimethyl oxalate.*



3 : 5-Dicarb-methoxy-4-di-2 : 2'-dihydroxy-diphenyl-Cyclopentan -1 : 2-dione :—Dry powdered dimethyl oxalate (5 g.) was shaken well under tap, with pure sodium methylate (2 g. sodium in 5 c.c. of methyl alcohol). A solution of pure dimethyl ββ'-2 : 2'-dihydroxy-diphenyl glutarate in absolutely dry ether (2·5 g. in 23 cc.) was added slowly to the above mixture without allowing rise of temperature. The whole was shaken well with further quantity of dry ether until

the mass became homogeneous. The excess of ether was then removed, and the residue was refluxed in a dry atmosphere at 120°-140° for 48 hours in an oil bath. It was then ground with ice-cold HCl. The brownish solid which separated was washed with sodium bicarbonate solution and water. Short colourless prisms from methyl alcohol m.p. 184° ; yield 20 p.c. (Found : C, 63·3 ; H, 4·4. $C_{21}H_{18}O_8$ requires C, 63·38 ; H, 4·5 per cent.). The compound was soluble in alcohol, acetone, ether and acetic acid ; sparingly soluble in benzene, chloroform, water and petroleum ; alcoholic solution gives a reddish coloration with $FeCl_3$.

The Diphenyl-Hydrazone :—The condensation product prepared above was dissolved in dilute acetic acid and mixed with a solution of phenyl-hydrazine in acetic acid (50 p.c.). The mixture was shaken well. The precipitate was separated by filtration and crystallised from alcohol. Yellowish needles, m.p. 128°; yield 40 p.c. (Found : N, 9·61 ; $C_{33}H_{30}O_6N_4$ requires N, 9·70 per cent.). On decomposing this with cold dilute HCl, the original condensation product was obtained.

(7) *Condensation with dimethyl phthalate.*

6 : 7-Benzo-1 : 5 diketo-2 : 4-carbmethoxy-3-di (2 : 2′ dihydroxyphenyl)-cycloheptane.

Dimethyl $\beta\beta'$-2 : 2′-dihydroxy-diphenyl glutarate (17·2 g.) was mixed intimately with dimethyl phthalate (9·7 g.) and dry methyl alcohol (3 cc.). Sodium wire (2·5 g.) was gradually dissolved in the mixture, which was then refluxed between 140° and 160° in an oil bath for about 5 hours. After cooling, the yellowish pasty mass in the flask was treated with dilute sulphuric acid in cold. The solid which separated was washed with excess of water and was kept with sodium bicarbonate solution for some hours in a refrigerator. Colourless prismatic crystals from absolute alcohol, m.p. 148°; yield, 25 p.c. (Found : C, 68·64 ; H, 4·72 ; $C_{27}H_{22}O_8$ requires C, 68·35 ; H, 4·64 per cent).

The diphenyl-hydrazone :—Bright yellowish needles from alcohol, m.p. 199° ; decomposition by dilute HCl in cold produced the original condensation product. (Found : N, 8·42 : $C_{39}H_{34}O_6N_4$ requires N, 8·53 per cent.).

The work is being continued.

We are greatly obliged to Dr. Wheeler, Principal, Royal Institute of Science, Bombay, for the profound interest and encouragement that he has had in the progress of this work.

TABLE OF COMPOUNDS.

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m.p. or b.p.	Analysis.	
				Calc.	Found.
Anhydride of $\beta\beta$-2 : 2′-dihydroxy-diphenyl-glutaric acid.	$C_{17}H_{14}O_{5}$	Heating the glutaric acid at 239° for an hour and distilling the residue at 40 mm. Yield, 80 p.c.	Small prismatic crystals from acetone and petroleum ether; m.p. 80°. Soluble in dilute alkali and gives the original glutaric acid by hydrolysis.	C. 68·45 H. 4·7	C, 68·26 H. 4·6
Diacetyl derivative of the anhydride.	$C_{21}H_{18}O_{7}$	(*i*) Keeping the glutaric acid with acetyl chloride in a dry atmosphere for 40 hours; yield, 55 per cent. (*ii*) Boiling the solution of the glutaric acid in acetic anhydride with anhydrous sodium acetate; yield, 50 p.c.	Long silky needles from acetic acid; m.p. 203° Hydrolysis with KOH yields the glutaric acid.	C, 66·0 H, 4·7	C, 65·66 H, 4·52
Dibenzoyl derivative of the anhydride.	$C_{31}H_{22}O_{7}$	(*i*) Action of benzoyl chloride on the anhydride	Prismatic crystals from alcohol. m.p. 167°. Hy-	C. 73·5 H, 4·35	C, 73·72 H. 4·53

		in pyridine ; yield quantitative. (*ii*) Heating the corresponding dibenzoyl glutaric acid at its m.p.	drolysis reproduces the glutaric acid.		
Imide from the anhydride.	$C_{17}H_{15}O_4N$	Heating the anhydride with liquor ammonia in a sealed carius tube at 150° for six hours ; yield, 40 p.c.	Yellow thick liquid, b.p. 135°\40 mm. Stable in solution with dilute alkali.	N, 4·71	N, 4·80
$\beta\beta'$-2 : 2'-Dibenzoyl diphenyl glutaric acid.	$C_{31}H_{24}O_8$	Action of benzoyl chloride on $\beta\beta$-2 : 2'-dihydroxy-diphenyl-glutaric acid in NaOH solution ; yield, 60 p.c. Gives a stable insoluble silver salt.	Small prismatic needles ; m.p. 223° (decomp). Hydrolysed to the dihydroxy glutaric acid by heating with conc. NaOH.	Eq. wt. 262 C, 70·99 H, 4·58	Eq. wt. 261·00 C, 70·69 H, 4·52
$\beta\beta'$-2 : 2'-dimethoxy-diphenyl glutaric acid.	$C_{19}H_{20}O_6$	(*i*) Action of methyl iodide on the dihydroxy glutaric acid in presence of NaOME, yield, 15 p.c.	Silky needles from alcohol ; m.p. 154° (decomp.). Forms a stable and insoluble silver salt.	Eq. wt. 172 C, 66·27 H, 5·81	Eq. wt. 172·5 C, 66·10 H, 5·74

TABLE OF COMPOUNDS.—(Contd.)

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m. p. or b. p.	Analysis Calc.	Analysis Found.
		(*ii*) Heating an alkaline solution of the dihydroxy glutaric acid with dimethyl sulphate and hydrolysis of the syrup thus obtained; yield, 25 p.c.			
$\beta\beta'$-2 : 2'-Dimethoxy-diphenyl glutaric anhydride.	$C_{19}H_{18}O_5$	Heating the corresponding dimethoxy glutaric acid at its m.p.; yield 50 p.c.	Colourless needles from alcohol; m.p. 160°. Boiling with conc. alkali generates the original acid.	C, 69·93 H, 5·52	C. 69·77 H, 5·48
Diethyl $\beta\beta'$-2 : 2'-dihydroxy - diphenyl-glutarate.	$C_{21}H_{24}O_6$	Heating the solution of the corresponding glutaric acid in absolute ethyl alcohol saturated with dry HCl gas and after removal of alcohol, diluting the residue with water; yield, 60 p.c.	Prismatic plates from dilute alcohol, m.p. 145°. Gives green coloration in alcoholic solution with $FeCl_3$. Hydrolysed to the acid by alcoholic potash.	C, 67·75 H, 6·45	C, 67·64 H, 6·51

Dimethyl-$\beta\beta'$-2 : 2' dihydroxy - diphenyl - glutarate.	$C_{19}H_{20}O_6$	Heating the solution of the glutaric acid in methyl alcohol saturated with dry HCl gas. Yield, 75 p.c.	White prisms from dilute alcohol, m.p. 189°. Hydrolysed to the glutaric acid, by heating with alcoholic KOH.	C. 65·89 H, 6·07	C, 66·03 H, 5·92
Diacetyl derivative of the above compound.	$C_{23}H_{24}O_8$	Keeping the ester with acetyl chloride in a dry atmosphere; yield, 60 p.c.	Oblong plates from dilute alcohol; m.p. 107°. Hydrolysed to the corresponding dihydroxy glutaric acid by alcoholic KOH.	C, 64·49 H, 5·6	C, 64·55 H, 5·65
Dibenzoyl derivative of the dimethyl ester.	$C_{33}H_{28}O_8$	Action of benzoyl chloride on the dihydroxy ester in pyridine; yield, 45 p.c.	Glistening needles from benzene; m.p. 152°. Hydrolysed to the corresponding dihydroxy glutaric acid by alcoholic KOH.	C, 71·74 H, 5·07	C, 71·55 H, 5·18
Dimethoxy derivative of the dimethyl ester.	$C_{21}H_{21}O_6$	Action of methyl iodide on pure dry dimethyl ester, in the presence of NaOME; yield 18 p.c.	Small needles from methyl alcohol m.p. 85°. Hydrolyses to the corresponding dimethoxy glutaric acid by alcoholic KOH.	C, 67·75 H, 6·48	C, 67·97 H, 6·58

TABLE OF COMPOUNDS.—(Contd.)

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m.p. or b.p.	Analysis.	
				Calc.	Found.
Dimethyl-ββ'-2 : 2'-dihydroxy - 3 : 3'. 5 : 5'-tetra bromo-diphenyl - glutarate.	$C_{19}H_{16}O_6Br_4$	Action of dry bromine on the dimethyl ester in acetic acid solution; yield, 70 p.c.	Colourless needles from acetic acid; m.p. 214°; with conc. HNO_3 it yields *2 : 4 di-bromo-o-nitrophenol*; m.p. 117°; identical with that of Bedroux (C. R. *126*, 1285).	Br. 48·49	Br. 48·40
ββ'-2 : 2'-Dihydroxy-5 : 5' dibromo-di-phenyl-glutaric acid.	$C_{17}H_{14}O_6Br_2$	Adding solution of bromine in acetic acid to a solution of the corresponding dihydroxy glutaric acid in acetic acid; yield, 40 p.c.	Colourless prisms from dilute alcohol; m.p. 180° (decomp). Action of conc. HNO_3 gives 4-bromo-o-nitro-phenol; m.p. 88°; identical with that of Bedroux (loc. cit.)	Eq. wt. 137 Br. 33·75	Eq. wt. 135·6 Br. 33·79
ββ'-2 : 2'-dihydroxy-3 : 3'-5 : 5'-tetra-bromo - diphenyl - glutaric acid.	$C_{17}H_{12}O_6Br_4$	(*i*) Addition of bromine to an aqueous solution of the corresponding glutaric acid; yield, 60 p.c.	Prismatic crystals from dilute alcohol; m.p. 210° (decomp.) Action of conc. HNO_3 gives 2 : 4-dibromo-orthonitro phenol identical with that of Bedroux.	Eq. wt. 316 Br. 50·63	Eq. wt. 317·1 Br. 50·58

		(*ii*) Action of bromine (excess) on the corresponding glutaric acid in solution with acetic acid; yield, 65 p.c.			
Semianilide of ββ-2 : 2′ - dihydroxy-diphenyl glutaric acid.	$C_{23}H_{21}O_5N$	Heating the glutaric acid with aniline at 110°. Yield, 30 p.c.	Pinkish needles from alcohol; m.p. 120° (decomp). Stable in solution with dilute alkalies. Gives an insoluble silver salt.	Eq. wt. 391 N. 3·58	Eq. wt. 390·3 N. 3·44
Anil of ββ′-2 : 2′- dihydroxy - diphenyl-glutaric acid.	$C_{23}H_{19}O_4N$	(*i*) Heating the semi-anilide at its m.p. Yield, theoretical. (*ii*) Heating the corresponding glutaric acid with aniline at 130°-140°. (*iii*) Heating a solution of the glutaric anhydride in dry alcohol with aniline for 24 hours; yield, 20 p.c.	Small white prisms, m.p. 220°. It dissolves in dilute alkali and can be regenerated from this solution.	N. 3·75	N. 3·71
Dianilide of ββ-2 : 2′ dihydroxy - diphenyl-glutaric acid.	$C_{29}H_{26}O_4N_2$	(*i*) Heating the semi-anilide with aniline at 160°-180° for 3 hours; yield, 50 p.c.	Small colourless prisms from glacial acetic acid; m.p. 298°; soluble in conc. alkali.	N. 6·01	N. 5·95

TABLE OF COMPOUNDS.—(Contd.)

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m.p. or b.p.	Analysis. Calc.	Analysis. Found.
		(*ii*) Heating the corresponding glutaric acid with aniline (excess) at 180°.			
Mono-ammonium salt of $\beta\beta'$-2 : 2'-dihydroxy-diphenyl glutaric acid.	$C_{17}H_{19}O_6N$	Addition of a calculated quantity of standard solution of ammonia to an aqueous solution of the glutaric acid. Yield, 70 p.c.	Light yellowish prisms. Distillation of the salt at 20 mm. Yielded the imide identical with that obtained from glutaric anhydride (loc. cit.).	Eq. wt. 333 N. 4·2	Eq. wt. 333·4 N. 4·07
Dibenzoyl derivative of the imide of $\beta\beta$-2 : 2' dihydroxy diphenyl - glutaric acid.	$C_{31}H_{23}O_6N$	Action of benzoyl chloride on the imide in pyridine; yield, 40 p.c.	White needles from alcohol; m.p. 61°.	C. 73·65 H. 4·55	C. 73·52 H. 4·63
$\beta\beta'$-2 : 2'-Dihydroxy-3 : 3' - dimethyl-diphenyl - glutaric acid.	$C_{19}H_{20}O_6$	Condensation of acetone dicarboxylic acid with o-cresol in the proportion of 1 : 2 mols. respectively in	Pinkish prisms from alcohol; m.p. 203° (decomp). Action of conc. sulphuric acid produced 8-methyl-	Eq. wt. 172 C. 66·3 H. 5·8	Eq. wt. 171·8 C. 66·2 H. 5·60

		the presence of 75 p.c. sulphuric acid ; yield, 20 p.c.	coumarin-4-acetic acid m. p. 184° (decomp) Eq. wt. 218·6 identical with that of Dey (loc. cit.) and o-cresol identified by its 4 : 6-dibromo derivative ; m.p. 57°.		
Copper salt of the acid above.	$C_{19}H_{18}O_6Cu$, $-2H_2O$	Addition of copper acetate solution to a neutral solution of the corresponding glutaric acid in NaOH ; yield, theoretical.	Small green prisms, containing 2 mols. of water of crystallisation.	Cu. 14·29	Cu. 14·45
$\beta\beta'$-2 : 2'-Dimethoxy-5 : 5'-dimethyl-di-phenyl-glutaric acid.	$C_{21}H_{24}O_6$	Shaking together acetone dicarboxylic acid and pure p-cresyl methyl ether in sulphuric acid (75 p.c.) for 48 hours. The glutaric acid to be separated from the uncombined ether by dissolving in $NaHCO_3$ solution and extracting this solution with ether before acidifying with HCl ; yield, 25 p.c.	Translucent prisms from hot alcohol ; m.p. 164° (decomp) ; Action of conc. H_2SO_4 produced 6-methylcoumarin-4-acetic acid [m. p. 183° (decomp). Eq. wt. 217·4] identical with that obtained by Dey (loc. cit.) and 2-methoxy-5-methyl phenyl glutaconic acid. (see later).	Eq. wt. 186 C. 67·75 H. 6·45	Eq. wt. 186·2 C. 67·41 H. 6·33

TABLE OF COMPOUNDS.—(Contd.)

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m.p. or b.p.	Analysis. Calc.	Analysis. Found.
The copper salt of the acid above.	$C_{21}H_{22}O_6Cu$, $-2H_2O$	Addition of copper acetate to a neutral solution of the glutaric acid in alkali; yield, theoretical.	Greenish rhombic prisms.	Cu. 13·4	Cu. 13·7
β - 2 - Methoxy - 5 - methyl - phenyl glutaconic acid.	$C_{13}H_{14}O_5$	Action of conc. H_2SO_4 on the ββ'-2 : 2' -dimethoxy-5 : 5 dimethyl diphenyl glutaric acid; yield, 20 p.c.	Short colourless needles from water m.p. 82°; converted to 6-methyl-coumarin-4-acetic acid (loc. cit.) by the action of conc. H_2SO_4.	Eq. wt. 125 C. 62·4 H. 5·61	Eq. wt. 125·2 C. 62·22 H. 5·50
ββ' - 2 : 2' - 5 : 5' tetra-hydroxy - di-phenyl glutaric acid.	$C_{17}H_{16}O_8$	Condensation of quinol with acetone dicarboxylic acid with shaking in sulphuric acid (75 p.c.). The un-reacted quinol was separated by filtration of the reaction mixture before pouring over ice; yield 15 p.c.	Yellowish coloured prisms; m.p. 242°-243° (decomp). Action of warm conc. H_2SO_4 converts it into 6-hydroxy - coumarin-4-acetic acid (m.p. 165°, Eq. wt. 220·2) identical with the compound obtained by Dey (loc. cit.) and a little quinol (m.p. 168°).	Eq. wt. 174 C. 58·6 H. 4·5	Eq. wt. 174·3 C. 58·6 H. 4·62
Copper Salt of the acid above.	$C_{17}H_{14}O_8Cu$, $-2H_2O$	Addition of copper acetate solution to a neutral solution of the glutaric acid in NaOH; yield, quantitative.	Bluish green plates containing 2 mols of water of crystallisation.	Cu. 14·16	Cu. 14·38

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CONDENSATION OF PHENOLS WITH ACETONE-DICARBOXYLIC ACID

Anhydrides of β-2-hydroxyphenyl glutaconic acids

BY

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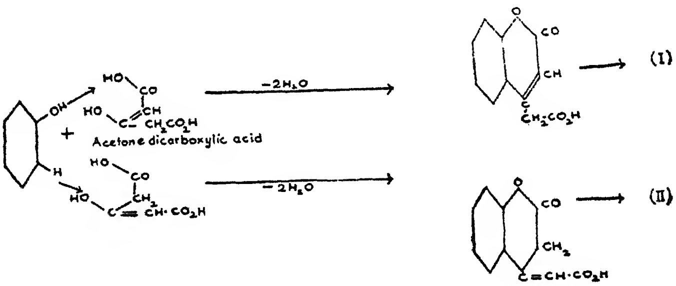
Coumarin-4-acetic acids have been prepared by condensing phenols with acetone-dicarboxylic acid in the presence of conc. sulphuric acid. [See:—Dey (Trans. Chem. Soc. 1915, *107,* 1606), Dey and Row (J. Ind. Chem. Soc. 1924, *I,* 110), Limaye (J. Ind. Chem. Soc. 1927, *IV,* 159) and Dixit (J. Ind. Chem. Soc. 1931, *VIII,* 787)]. In some of his reactions, Dey has obtained tautomers (I and II) of the same coumarin-4-acetic acid supposed to be formed at the same time due to the two different ways in which the acetone-dicarboxylic acid may act. The reaction is represented as follows :—



Transformation of (II) to (I) was supposed to take place in the process of crystallisation which invariably caused a considerable change in the m.pts. The two forms had the same equivalent and analytical data and both produced the corresponding 4-methyl coumarin when heated at their m.pts. Other experimental evidence to show the existence of (II) has not been recorded and the conversion of (I) to (II) has not been carried out.

With the object of studying the reaction in details, phenol and the three cresols were condensed with acetone-dicarboxylic acid on the lines described by Dey and Row (loc. cit.) as the results from this method and from that of Dey (loc. cit.) were identical. The crude product of each of these reactions, when fractionally crystallised, yielded two different compounds (A) and (B), which were partly transformed into one another on long exposure to air.

The substance (A) of lower m.pt.

(1) Crystallises in long needles soluble in hot water, dilute alcohol, ether and in sodium bicarbonate solution with effervescence. The original compound is recovered on acidifying this solution.

(2) Does not give any coloration with $FeCl_3$ and does not form any definite compound with (*i*) acetyl chloride or acetic anhydride, (*ii*) benzoyl chloride, and (*iii*) oxidation by chromic acid in cold.

(3) Yields quantitatively the corresponding 4-methyl coumarin, when heated at its m.pt.

(4) Forms the solid ethyl ester which in turn condenses with salycilic aldehyde in the presence of piperidine to produce the corresponding dicoumaryl [see Dey and Row (loc. cit.)].

In short, the substance (A) agrees well with the corresponding coumarin-4-acetic acid, found in literature.

The substance (B) of higher m.pt.

(1) Crystallises in broad prismatic needles, insoluble in water and dilute alcohol; soluble in alcohol, acetone and chloroform. Insoluble in sodium bicarbonate unless being in contact with it for a long time.

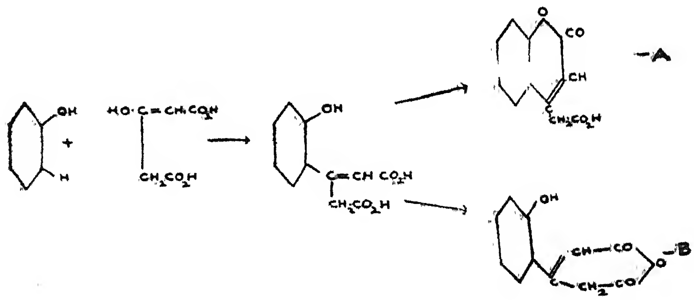
(2) Gives, in alcoholic solution, reddish coloration with $FeCl_3$.

(3) Can be titrated in alcoholic solution with alkali and has the same equivalent and analytical data as those of substance (A).

(4) Does not form an ester and does not condense with salycilic aldehyde under dry conditions.

Constitution of (B).—The compound (A) can be converted into (B) by keeping it in contact with conc. H_2SO_4. The reverse change proceeds on hydrolysis of (B) by alkali.

The compound (B) is supposed to be the anhydride of the corresponding ortho substituted glutaconic acid, formed as follows :—



β-2-Hydroxyphenyl-
glutaconic acid.

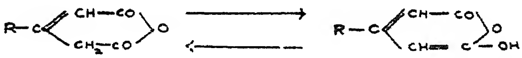
The intermediate glutaconic acid is known to be incapable of free existence.

The following evidence is found in literature to justify this course of the condensation :—

(1) β-Substituted glutaconic acids have been prepared by condensing phenols and phenolic ethers with acetone dicarboxylic acid in the presence of conc. sulphuric acid. [See Limaye and Bhave (J. Ind. Chem. Soc. 1931, VIII, 137.) Dixit (J. Ind. Chem. Soc. 1931, VIII, 787.) Limaye and Gogate (Proc. Ind. Sc. Congress, 1932, p. 233). The corresponding coumarin-4-acetic acids were also found as by-products.]

(2) Elimination of water from glutaconic acid under the influence of sulphuric acid is quite likely to proceed in two ways as shown above.

(3) The substance (B) acts as a mono-basic acid on account of its transformation into the "Hydroxy anhydride" due to the mobility of a hydrogen atom as explained by Thorpe [see Thorpe and Thole (Trans. Chem. Soc. 1911, *99*, 2187). Thorpe and Bland (Trans. Chem. Soc. 1912, *101*, 867)].



Normal anhydride. Hydroxy anhydride.

The following experiments were further carried on with the substance (B), and their results agree with the constitution assumed for it.

(1) Benzoylation.—Action of benzoyl chloride on the compound in solution with pyridine produces a neutral dibenzoyl derivative which is hydrolysed by alkali to the corresponding coumarin-4-acetic acid.

(2) Elimination of CO_2.—By decomposing the compound under specially dry conditions, and reduced pressure, a phenolic substance results which sublimes and lowers the m.p. of the corresponding 4-methyl coumarin when mixed with it.

(3) Oxidation of the substance in solution with acetic acid by chromic acid yields the corresponding ortho-hydroxy-benzoic acid.

(4) Action of acetic anhydride in presence of sodium acetate on the substance, gives a crystalline acidic compound which is supposed to be formed according to the reaction described by Gabriel and Neumann (Ber. 1893, *26*, 951). The nature of this reaction is still under investigation.

The results obtained so far seem to indicate that the crystallisation of the crude product of higher m.p. into coumarin-4-acetic acid of lower m.p. as reported by Dey (loc. cit.) in some cases, may be due to the partial conversion of the substance of (B) type into that of (A) under those conditions.

Further work is in progress.

EXPERIMENTAL

Condensation of phenol with acetone-dicarboxylic acid Coumarin-4-acetic acid.

Pure citric acid (25 g.) was heated with conc. sulphuric acid (40 cc.) at 60°-70° till complete elimination of carbon monoxide. Phenol (10 g.) was added to the mixture and it was kept overnight. It was then poured over ice (100 g.) and the solution was thoroughly extracted with ether. The ethereal solution was dried and after removal of ether the residue was shaken with *absolute alcohol and filtered,* the filtrate being carefully collected. The solid on the filter was then washed with water and crystallised from dilute alcohol; long white silky needles, m.p. 168° (decomp); yield, 12 p.c., mixed with coumarin-4-acetic acid prepared by the process of Limaye (*loc. cit.*) melts at 169° (decomp). (Found:—Eq. wt. 203·5; C, 64·59; H. 3·98; $C_{11}H_8O_4$ requires Eq. wt. 204; C, 64·71; H, 3·92 per cent. When heated at its m.p. it produced *4-methyl coumarin*; m.p. 79°. Boiling the solution of the acid in ethyl alcohol with a little quantity of conc. sulphuric acid, gives the *ethyl ester*; m.p. 116°. When the ester was condensed with salycil-aldehyde according to the method of Dey and Row (*loc. cit.*) *the corresponding dicoumaryl* (m.p. 246°.) was obtained. These compounds were identified with those already found in literature.

2-Hydroxy-phenyl-glutaconic anhydride.

(*i*) The alcoholic filtrate obtained above was diluted with water and the compound which separated was filtered, washed with sodium bicarbonate solution and water, and crystallised from absolute alcohol. Short prismatic needles; m.p. 188° (decomp); yield, 15 p.c. (Found :—Eq. wt. 202·2; C, 64·56; H, 3·80. $C_{11}H_8O_4$ requires Eq. wt. 204, C, 64·71; H, 3·92 p.c.) Alcoholic solution gives reddish coloration with Ferric chloride. Similar results were obtained on carrying out the condensation with free acetone dicarboxylic acid (15 g.) and the same proportions of phenol and sulphuric acid.

(*ii*) *Conversion of Coumarin-4-acetic acid to β-2-hydroxy-phenyl-glutaconic anhydride :—*

Coumarin-4-acetic acid (10 g.) was dissolved in sulphuric acid (100 cc. of 100 p.c.) and the solution kept overnight in an evacuated

desiccator. It was then poured over ice (250 g.) and the solution extracted with ether. After removing ether, the residue was washed with $NaHCO_3$ solution and water and was crystallised from absolute alcohol. Prismatic needles, m.p. 188° (decomp) ; yield 60 p.c. Mixture with the compound obtained directly in the condensation (described above) melts at 187° (decomp).

(*a*) *Conversion of β-2-hydroxy-phenyl glutaconic anhydride to the coumarin-4-acetic acid.*

The gutaconic anhydride (5 g.) was dissolved in sodium hydroxide solution (50 cc. of 20 p.c.) and the solution refluxed for 2 hours. It was acidified by HCl after cooling and the precipitate separated by filtration. It was dissolved in sodium bicarbonate solution, reprecipitated by HCl and finally crystallised from dilute alcohol. White silky needles ; m.p. 168° (decomp) ; yield, 75 p.c.

(*b*) *Oxidation* :—β-2-Hydroxy phenyl glutaconic anhydride (5 g.) was dissolved in glacial acetic acid (40 cc.) and chromic acid (2·5 g.) with a few drops of conc. H_2SO_4, were added to the solution. The mixture was heated at 50° on a water bath, for half an hour, and then poured into water. The solution was extracted with ether, the ether removed, and the residue was crystallised from dilute alcohol : white silky needles, m.p. 152° ; yield, 12 p.c. Mixed with *salicylic acid* ; m.p. 154°. (Found.—Eq. wt. 138·2 ; $C_7H_6O_3$ requires Eq. wt. 138.).

(*c*) *Elimination of CO_2* :—β-2-Hydroxy-phenyl-glutaconic anhydride (4 g.) was heated at 188° at 20 mm. pressure under perfectly dry conditions. The sublimate was collected and crystallised from absolute alcohol ; small leaflets, m.p. 82° ; yield, 25 p.c. Forms a yellowish solution with alkali. Mixture with the 4-methyl coumarin melts between 70°-76°. Gives green coloration with ferric chloride in alcoholic solution. The compound is still under investigation.

(*d*) *The dibenzoyl derivative* :—

β-2-Hydroxy-phenyl-glutaconic anhydride (5 g.) was dissolved in pyridine (20 cc.) and the solution shaken with benzoyl chloride (4 cc.) avoiding rise in temperature, for about half an hour. Pyridine was removed by treating the solution with dilute HCl. The residue was separated by filtration, washed with sodium bicarbonate solution and water and finally crystallised from acetic acid. Small yellowish needles ; m.p. 252°. Yield 60 p.c. (Found : C, 72·68 ; H, 4·04 ; $C_{25}H_{16}O_6$ requires C, 72·81 ; H, 3·88 per cent).

Hydrolysis of the dibenzoyl derivative (2 g.) with alcoholic potash (50 cc. of 30 p.c.) produced coumarin-4-acetic acid ; long needles : m.p. 170° (decomp). Yield, 30 p.c. Mixture with known coumarin-4-acetic acid melts at 169° (decomp).

Similar sets of compounds obtained by the condensations of the three cresols with acetone dicarboxylic acid, will be found in the adjoining tables.

We owe a good deal to Dr. Wheeler, Principal of the Royal Institute of Science, Bombay, for the progress of the work so far and we have the pleasure to record our thanks to him.

TABLE OF COMPOUNDS.

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m.p. or b.p.	Analysis. Calc.	Analysis. Found.
7-Methyl - coumarin-4-acetic acid.	$C_{12}H_{10}O_4$	(*i*) Condensation of acetone - dicarboxylic acid with meta-cresol. Fractional crystallisation of the condensation product; yield, 60 p.c. (*ii*) Boiling β-2-hydroxy-4-methyl phenyl glutaconic anhydride with NaOH; yield, 70 p.c.	Long white needles; m.p. 168° (decomp). Gives 4 : 7-dimethyl coumarin (m.p. 132°) by elimination of CO_2 at m.p. and the ethyl ester (m.p. 131°) by boiling with ethyl alcohol in presence of a little of conc. H_2SO_4. The ester gives, with salycilic aldehyde-7-methyl - 4 : 5 dicoumaryl; m.p. 247°.	Eq. wt. 218 C. 66·06 H. 4·58	Eq. wt. 218·6 C. 65·98 H. 4·48
β - 2-Hydroxy - 4 - methyl - phenyl - glutaconic anhydride.	$C_{12}H_{10}O_4$	(*i*) Condensation of acetone dicarboxylic acid with meta-cresol; yield, 35 p.c. (*ii*) Keeping 7-methyl-coumarin-4-acetic acid in sulphuric acid (100 p.c.) in evacuated desiccator overnight; yield, 90 p.c.	Short prisms from alcohol; m.p. 212° (decomp). Insoluble in $NaHCO_3$ solution. On elimination of CO_2 at reduced pressure, it gives a sublimatory phenolic crystalline product; m.p. 110°; mixed	Eq. wt. 218 C. 66·06 H. 4·58	Eq. wt. 220·2 C. 66·13 H. 4·61

TABLE OF COMPOUNDS.—(Contd.)

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m.p. or b.p.	Analysis.	
				Calc.	Found.
			with 4 : 7-dimethyl coumarin, m.p. 97°.		
2-Hydroxy 4-methyl benzoic acid.	$C_8H_8O_3$	Oxidation of 2-hydroxy-4-methyl-phenyl glutaconic anhydride with chromic acid, in acetic acid solution ; yield, 20 p.c.	Silky needles from dilute alcohol ; m.p. 173°. Mixed with the known acid prepared according to the method of Schall (Ber. *12*, 820) ; m.p. 172°.	Eq. wt. 152·0	Eq. wt. 151·8
Dibenzoyl derivative of the glutaconic anhydride.	$C_{26}H_{18}O_6$	Action of benzoyl-chloride on the glutaconic anhydride in solution with pyridine ; yield, 70 p.c.	Small white needles from acetic acid ; m.p. 275°. Insoluble in alkali solutions. On boiling with conc. alkali, it hydrolyses to 7-methyl - coumarin-4-acetic acid ; m.p. 168° (decomp).	C. 73·24 H. 4·23	C. 73·18 H. 4·17
6-Methyl - coumarin-4-acetic acid.	$C_{12}H_{10}O_4$	(*i*) Condensation of acetone dicarboxylic acid with para-cresol. Fractional	White needles from dilute alcohol ; m.p. 173° (decomp). On elimination	Eq. wt. 218 C. 66·06 H. 4·58	Eq. wt. 217·5 C. 65·92 H. 4·67

		crystallisation of the cond. product. Yield, 40 p.c. (*ii*) Boiling β-2-hydroxy-5-methyl phenyl glutaconic anhydride with NaOH; yield, 80 p.c.	of CO_2 at m.pt. It gives 4 : 6-dimethyl coumarin; m.p. 148°.		
β-2 - Hydroxy - 5 - methyl phenyl glutaconic anhydride.	$C_{12}H_{10}O_4$	(*i*) Condensation of acetone-dicarboxylic acid with para-cresol; yield, 55 p.c. (*ii*) Keeping 6-methyl-coumarin-4-acetic acid in sulphuric acid (100 p.c.) overnight; yield, 80 p.c.	Prismatic needles from absolute alcohol; m.p. 192° (decomp). Insoluble in $NaHCO_3$ solution. Elimination of CO_2 under reduced pressure gives the sublimatory, crystalline phenolic substance: m.p. 155°; mixed with 4 : 6 dimethyl-coumarin; m. p. 142°.	Eq. wt. 218 C. 66·06 H. 4·58	Eq. wt. 206·8 C. 66·24 H. 4·71
2-Hydroxy - 5 - methyl-benzoic acid.	$C_8H_8O_3$	Oxidation of β-2-hydroxy-5-methyl-phenyl glutaconic anhydride with chromic acid in solution with acetic acid; yield, 15 p.c.	Long thin needles from alcohol; m.p. 148°. Mixed with known compound m.p. 146·5°.	Eq. wt. 152	Eq. wt. 152·4

TABLE OF COMPOUNDS.—(Contd.)

Name.	Formula.	Method of Formation and Yield.	Appearance, properties m.p. or b.p.	Analysis. Calc.	Analysis. Found.
Dibenzoyl derivative of the β-2-hydroxy-5-methyl - phenyl glutaconic anhydride.	$C_{26}H_{18}O_6$	Action of benzoyl chloride on the glutaconic anhydride in solution with pyridine ; yield, 65 p.c.	Small prismatic needles from glacial acetic acid ; m.p. 310°. Hydrolysed to 6-methyl - coumarin-4-acetic acid by boiling with alkali m.p. 173° (decomp).	C. 73·24 H. 4·23	C. 73·11 H. 4·01
8-Methyl coumarin-4-acetic acid.	$C_{12}H_{10}O_4$	(*i*) Condensation of acetone dicarboxylic acid with ortho-cresol. Cond. product separates on keeping the mixture in Refrigerator overnight ; Yield, 25 p.c. (*ii*) Boiling β-2-hydroxy-3-methyl phenyl glutaconic anhydride with NaOH ; yield, 75 p.c.	Short needles from dilute alcohol ; m.p. 182° (decomp) ; Elimination of CO_2 at m.pt. gives 4 : 8-dimethyl coumarin ; m.p. 118°.	Eq. wt. 218 C. 66·06 H. 4·58	Eq. wt. 218·3 C. 66·00 H. 4·42
β - 2 - Hydroxy - 3 - methyl phenyl glutaconic anhydride.	$C_{12}H_{10}O_4$	(*i*) Condensation of acetone dicarboxylic acid with ortho-cresol. Fractional	Prismatic short needles from acetone m.p. 188° (decomp). Elimination of	Eq. wt. 218 C. 66·06 H. 4·58	Eq. wt. 209·3 C. 66·24 H. 4·51

		crystallisation of the cond. product ; Yield, 30 p.c. (*ii*) Keeping 8-methyl-coumarin-4-acetic acid in sulphuric acid (100 p.c.) overnight ; yield, 70 p.c.	CO_2 under reduced pressure gives the crystalline phenolic sublimate ; m.p. 120° ; mixed with 4 : 8-dimethyl coumarin, m.p. 107°.		
2-Hydroxy 3-methyl benzoic acid.	$C_8H_8O_3$	Oxidation of β-2-hydroxy-5-methyl - phenyl - glutaconic anhydride with chromic acid ; yield, 25 p.c.	Long needles from alcohol ; m.p. 158°. Mixed with the known compound ; m. p. 156°.	Eq. wt. 152	Eq. wt. 151·6
Dibenzoyl derivative of the β-2-Hydroxy-3-methyl phenyl glutaconic anhydride.	$C_{26}H_{18}O_6$	Action of benzoyl chloride on the glutaconic anhydride in solution with pyridine ; yield, 62 p.c.	Leaflets from glacial acetic acid m.p. 288°. Hydrolysed to 8-methyl coumarin-4-acetic acid by boiling with alkali ; m.p. 181°. (decomp.)	C. 73·24 H. 4·23	C. 73·09 H. 4·11

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STUDY OF THE ACTION OF SODIUM AND POTASSIUM ON COMPOUNDS CONTAINING THE -NH- GROUP

BY

S. V. SHAH AND D. G. PISHAVIKAR

Various methods have been used to replace the hydrogen of the -NH- group in acetylated as well as non-acetylated amines by sodium or potassium. (*a*) Metallic sodium at high temperature : Heydreh, Ber. 1885-*18*, 2156 ; Belart D. R. P. 207981 ; C. 1909, 1, 1283 ; Titherley J. C. S. 1897, 463. (*b*) Sodiumethoxide : Chattaway and Ingle J. C. S. 1895, 1090. (*c*) Sodamide : Titherley (loc. cit.). (*d*) Sodium amalgam : Wheeler, American Chemical J. *23*, 464. (*e*) Sodium in boiling xylene : Bunge A Supp. *7*, 122). We have tried to prepare the Sodium and Potassium derivatives by the action of Sodium and Potassium in boiling Toluene on various substances.

In continuation of our previous work (Journal of the University of Bombay, 1932, Vol. I, Part 2, page 31) using the same methods both preparative and analytical, we have now succeeded in preparing the Sodium and Potassium compounds given in the following tables. These compounds are micro-crystalline and insoluble in ordinary organic solvents and are quantitatively decomposed into sodium hydroxide or Potassium hydroxide and the original substance by the action of boiling water for a short time. Under the same conditions it was not possible to prepare the Sodium or Potassium Compounds of (*i*) Diphenylamine, (*ii*) Methylaniline, (*iii*) Ethylaniline, (*iv*) Benzylaniline, (*v*) Carbazole and (*vi*) Indole.

In view of the fact that some of the above named compounds 1-6 (*viz.*, Carbazole and diphenylamine) do form Sodium derivatives under other sets of conditions, we do not propose for the present to suggest any final explanation for the difference in the behaviour of these compounds towards Sodium and Potassium.

EXPERIMENTAL

Table No. I.

Potassium Derivatives

Name of the Compound.	Quantities of the amide and potassium taken.	M. P.	Found.	Calculated for.	Remarks.
I. Potassium acet - m - toluidide.	1·5 gms. & 0·3 gm. respectively.	146°C	K; 20·56% (estimated as K_2SO_4); K; 20·67% (Volumetrically) N; 7·55%.	$C_9H_{10}ONK$ K; 20·85% N; 7·48%	
II. Potassium Methyl - acet-amide.	1·46 gms. & 0·78 gm. respectively.	——	K; 35·18% (estimated as K_2SO_4). K; 35·10% (Volumetrically). N; 12·68%.	C_3H_6ONK K; 35·13% N; 12·60%	
III. Potassium di-acetamide.	2·02 gms. & 0·78 gm. respectively.	——	K; 28·11% (estimated as K_2SO_4). K; 28·12% (Volumetrically). N; 10·10%.	$C_4H_6O_2NK$ K; 28·05% N; 10·06%	
IV. Potassium carbanilide.	2·12 gms. & 0·78 gm. respectively.	——	K; 15·47% (estimated as K_2SO_4). K; 15·72% (Volumetrically). N; 11·24%.	$C_{13}H_{11}N_2OK$ K; 15·60% N; 11·20%	
V. Di-Potassium oxanilide.	1·2 gms. & 0·39 gm. respectively.	——	K; 24·56% (estimated as K_2SO_4). K; 24·85% (Volumetrically. N; 9·04%.	$C_{14}H_{10}N_2O_2K_2$ K; 24·68% N; 8·86%	

TABLE No. II.

Sodium Derivatives

Name of the Compound.	Quantities of the amide and sodium taken.	M. P.	Found.	Calculated for	Remarks.
1. Sodium acet -m-toluidide.	1·5 gms. & 0·23 gm. respectively.	——	Na ; 13·41% (estimated as Na_2SO_4). Na ; 13·51% (Volumetrically). N ; 8·23%.	$C_9H_{10}ONNa$ Na ; 13·45%. N ; 8·18%.	
II. Sodium-Methyl-acetamide.	1·46 gms. & 0·23 gm. respectively.	——	Na ; 24·27% (estimated as Na_2SO_4). Na ; 24·18% (Volumetrically). N ; 14·85%	C_3H_6ONNa Na ; 24·21% N ; 14·73%.	
III. Sodium-di-acetamide.	2·02 gms. & 0·46 gm. respectively.	——	Na ; 18·75% (estimated as Na_2SO_4). Na ; 18·72% (Volumetrically). N ; 11·49%.	$C_4H_6O_2NNa$ Na ; 18·70% N ; 11·38%	
IV. Sodium-carbanilide.	1·12 gms. & 0·46 gm. respectively.	——	Na ; 9·79% (estimatted as Na_2SO_4). Na ; 9·85%. Na ; 9·85% (Volumetrically). N ; 12·12%.	$C_{13}H_{11}N_2ONa$ Na ; 9·82% N ; 11·96%	
V. Di-Sodium Oxanilide.	1·2 gms. & 0·23 gm. respectively.	——	Na ; 16·14% (estimated as Na_2SO_4). Na ; 16·20%. (Volumetrically). N ; 9·97%.	$C_{14}H_{10}N_2O_2Na_2$ Na ; 16·19% N ; 9·85%	As stated above this compound has been prepared by Wheeler before, by the action of sodium amalgum on Oxanilide.

In the end we take this opportunity to thank the University of Bombay for a research grant which enabled us to conduct this piece of work.

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VISCOSITY OF MODERATELY AND HIGHLY CONCENTRATED SOLUTIONS OF SOME ELECTROLYTES IN WATER AND METHYL, ETHYL AND n-PROPYL ALCOHOLS AND A DISCUSSION OF RELATION BETWEEN CONDUCTANCE AND FLUIDITY

BY

H. N. DESAI*, D. B. NAIK AND B. N. DESAI

In a previous paper (H. N. Desai, D. B. Naik and B. N. Desai, Indian J. Physics, *8*, 323, 1934) we have given results of conductance of solutions of some electrolytes in water and methyl, ethyl and n-propyl alcohols. Simultaneous measurements of viscosity of those solutions at 30°C were also made with an Ostwald viscometer. In the present paper it is proposed to give some of the viscosity results of moderately and highly concentrated solutions and also to discuss the relation between conductance and fluidity.

The time required for the flow of solution between the two marks on the Ostwald viscometer was accurately noted by means of a previously calibrated stop watch reading upto one-tenth of a second. The time of flow for conductivity water was first determined to find out the constant of the viscometer. A number of readings were taken in each case and the mean value calculated. The density measurements were made by means of a pyknometer. The viscosity was calculated by using Poiseuille's formula. In the calculations the viscosity of water at 30°C was taken as 0·008007 dynes sec/cm^2.

RESULTS AND DISCUSSION

(*a*) *Relation between viscosity and concentration.*

It was found that in aqueous solutions chlorides, iodides and nitrates of potassium and ammonium show negative viscosity within a certain range of concentration with an increase in concentration of salt solution. The general nature of the viscosity-concentration (gram equivalent/litre-C) curves in these cases is similar to that

*The experimental work has been carried out entirely by Mr. H. N. Desai under the direction of the other two authors. The detailed results are to be submitted shortly in the form of a thesis for the M.Sc. degree of the Bombay University.

of the curves for KI and NH_4I given in Fig. 1. The results of KI agree within 1% with those of Getman (J. de Chem. Phys., *5*, 344, 1907.) and of KCl and NH_4Cl very closely with those of Simon

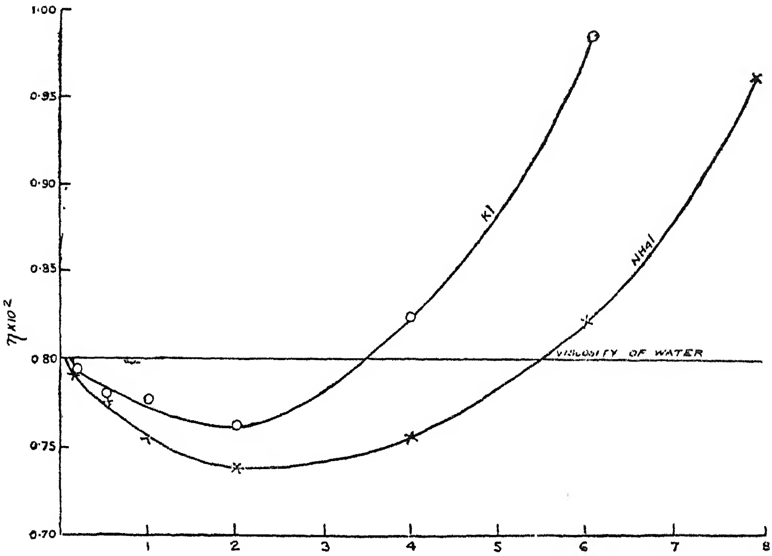

Fig. 1

(C. R., *176*, 437, 1923). In the case of methyl and ethyl alcohols only potassium and ammonium chlorides show negative viscosity (Figs. 2 and 3). In these cases it is observed that the range of

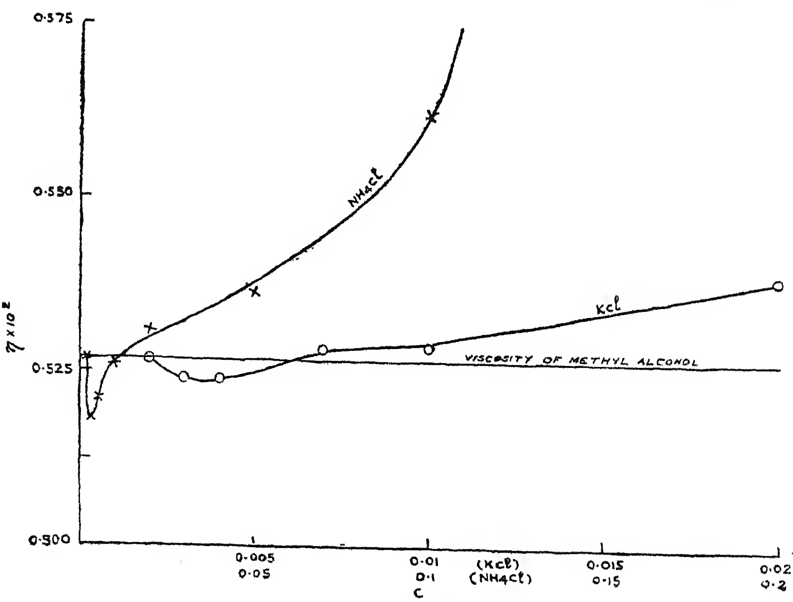

Fig. 2

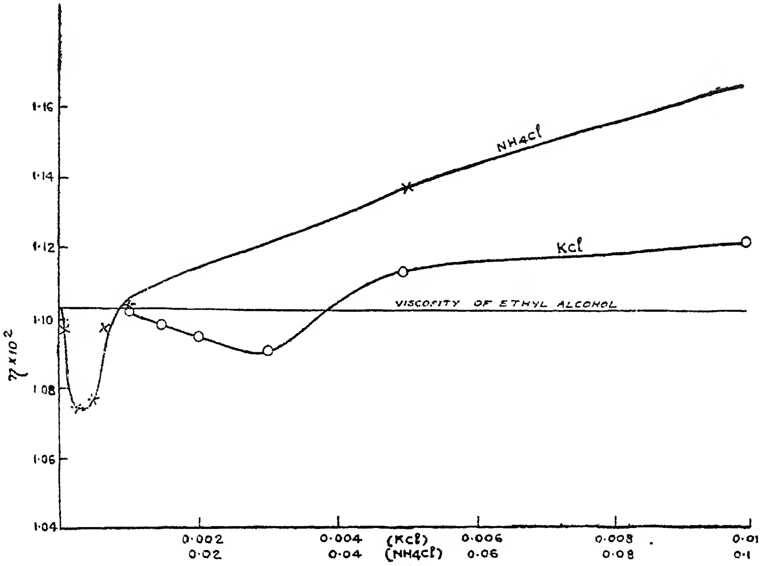

Fig. 3

concentration over which viscosity decreases with concentration as well as the extent of the decrease in the viscosity is much less than in the case of water. In n-propyl alcohol a tendency for negative viscosity is shown between concentrations 0·0008N and 0·002N.

In all the above cases of negative viscosity it has been observed by us (H. N. Desai, D. B. Naik and B. N. Desai, Current Science, *2*, 206, 1933) that the relative viscosity increases with concentration upto a certain stage in very dilute solutions, in agreement with the requirements of the Falkenhagen-Dole theory (Phys. Z., *30*, 611, 1929 ; also see Jones and Dole, Jour. Amer. Chem. Soc., *51*, 2950, 1929 ; Falkenhagen Phys. Z., *32*, 745, 1931 ; Joy and Wolfenden, Nature, *126*, 994, 1930 ; Proc. Roy, Soc., *314*, 413, 1932 ; Falkenhagen and Vernon, Phil. Mag., *14*, 537, 1932).

In Figs. 4 and 5 are plotted the results of viscosity against concentration of some other salts in water and methyl alcohol. It will be seen that the viscosity increases regularly with an increase in the concentration of the solution. Also salts which are very soluble show a very large increase in viscosity at high concentrations. The nature of curves for other salts used in these experiments (except those

which show negative viscosity) in all the four solvents is exactly similar to that of the curves given in Figs. 4 and 5.

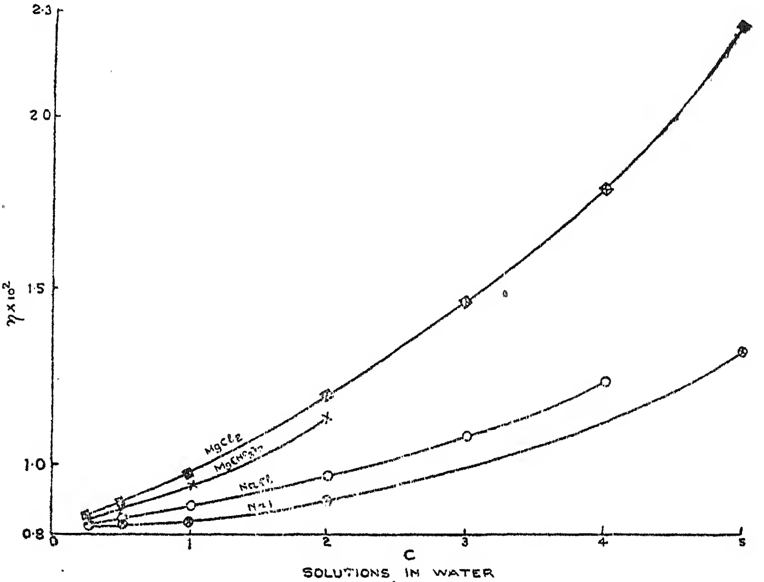

Fig. 4.

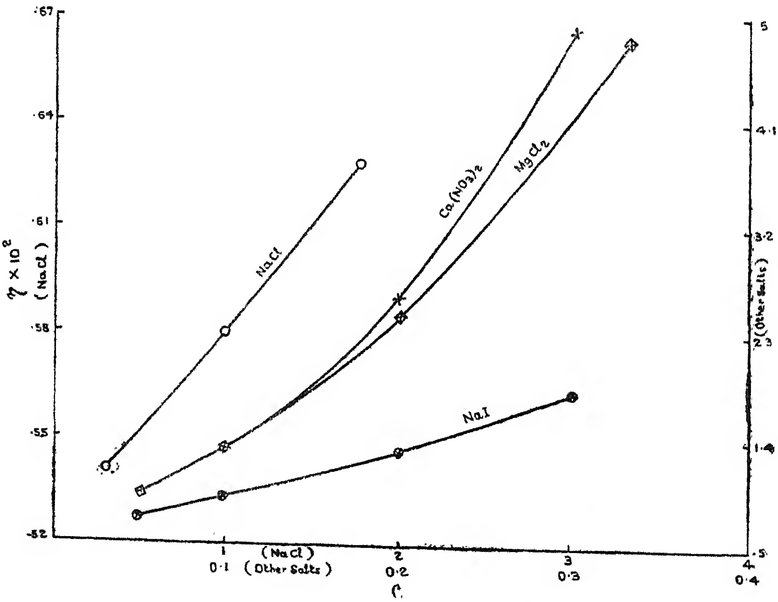

Fig. 5.

Grinnell Jones and Malendel Dole (Jour. Amer. Chem. Soc., 51, 2950, 1929) have proposed an equation connecting viscosity with concentration. They have stated that it is applicable only upto a concentration of 0·5 N in case of $BaCl_2$ in water. For other salts it is valid only for very dilute solutions (also see in this connection paper by Grinnell Jones and Talley, Jour. Amer. Chem. Soc., *55*, 4124, 1933). An attempt was made to fit in the results obtained in this investigation, in various types of equations and it was found that the following equation could be applied successfully over a wide range of concentration, especially in moderately and highly concentrated solutions :—

$$\eta_c = \eta_o + D_1C^2 + D_2C^3$$

where η_c and η_o are the viscosity of the solution and solvent respectively, C is concentration in gram equivalents per litre of solution and D_1 and D_2 are constants for the particular salt. In Table I are given the values of η_c calculated according to the above equation for some salts in different solvents. The values of constants D_1 and D_2 were calculated by the method of least squares.

TABLE I

	C.	$\eta_c \times 10^2$ Observed	$\eta_c \times 10^2$ Calculated.	$[\frac{\eta_c}{\eta_o}-1]/c$
	WATER			
NaI ...	7·9	2·6630	2·7432	0·294
	5·0	1·3310	1·4459	0·133
$D_1 = 0{\cdot}01661 \times 10^{-2}$ ...	2·0	0·8945	0·8818	0·059
	1·0	0·8285	0·8192	0·035
$D_2 = 0{\cdot}001839 \times 10^{-2}$ ...	0·5	0·8245	0·8051	0·060
	0·1	0·8194	0·8009	0·230
BaI_2 ...	3·2	1·0290	1·0433	0·089
	1·0	0·8480	0·8471	0·059
$D_1 = 0{\cdot}05674 \times 10^{-2}$ ...	0·5	0·8217	0·8136	0·052
	0·1	0·8048	0·8013	0·050
$D_2 = -\ 0{\cdot}01033 \times 10^{-2}$ ...	0·01	0·8019	0·8007	0·120

O

METHYL ALCOHOL

$CaCl_2$ ...	4·0	9·3970	8·9739	4·21
	3·0	5·0470	5·4931	2·86
$D_1 = 0{\cdot}6232 \times 10^{-2}$ ...	2·0	2·4650	2·8293	1·84
	1·0	1·2410	1·1263	1·35
$D_2 = -\ 0{\cdot}0238 \times 10^{-2}$ ...	0·5	0·8206	0·6827	1·11
	0·1	0·6141	0·5331	1·66
	0·05	0·5746	0·5285	1·82
	0·01	0·5400	0·5275	2·50

ETHYL ALCOHOL

$MgCl_2$ ...	2·9353	7·690	7·533	2·03
	2·0	4·676	5·918	1·62
	1·0	2·404	2·790	1·13
$D_1 = 2{\cdot}172 \times 10^{-2}$ ...	0·5	1·779	1·585	1·23
	0·1	1·272	1·124	1·53
$D_2 = -\ 0{\cdot}4855 \times 10^{-2}$ ...	0·05	1·191	1·108	1·60
	0·01	1·145	1·103	3·80

n-PROPYL ALCOHOL

NaI ...	0·6	2·531	2·5020	0·80
	0·1	1·877	1·9172	0·97
$D_1 = 24{\cdot}18 \times 10^{-2}$ ...	0·05	1·803	1·7559	1·08
	0·01	1·752	1·7124	2·40
$D_2 = -\ 36{\cdot}63 \times 10^{-2}$ ...	0·005	1·726	1·7106	1·80
$CaCl_2$ ...	2·0	12·220	13·4460	3·07
	1·0	4·816	5·6110	1·82
$D_1 = 5{\cdot}118 \times 10^{-2}$ ...	0·5	3·034	2·8369	1·55
	0·1	2·042	1·7600	1·93
$D_2 = -\ 1{\cdot}217 \times 10^{-2}$ ...	0·01	1·818	1·7105	6·30
	0·005	1·778	1·7101	8·00

It will appear from the Table that in all the cases there is on the whole a fairly good agreement between the observed and the calculated values of viscosity for concentrated salt solutions. A still better agreement between the observed and the calculated values can be obtained if in determining the values of constants one uses a very large number of observations taken at very short interval of concentrations. It will appear from the form of the equation that the term D_1C^2 is large when compared with the term D_2C^3 for relatively dilute solutions, while the term D_2C^3 is also important for higher concentrations.

In column 4 of Table I are also given the values of factor $[(\eta_c/\eta_o)-1]/C$ for some salts. It will be found that in all the cases given in the Table except NaI in n-propyl alcohol, a minimum value is found to occur. It will be obvious that the values of this factor for cases of negative viscosity will also show a minimum. The minimum in the viscosity increment-concentration values observed here thus supports the results of Grüneisen (Wiss, Abh. d. Phys., Tech. Reichsanst., *4*, 239, 1905), Appleby (Journ. Chem. Soc., *97*, 2000, 1910) and Merton (Journ. Chem. Soc., *97*, 2454, 1910). According to Grüneisen this effect might be due to dissociation of salt molecules in solution. The present results do not support the observation of Tower (Journ. Amer. Chem. Soc., *38*, 833, 1916) according to whom the values of the factor are tolerably constant for alcoholic solutions. The causes of a maximum in the values of the factor in the case of NaI in n-propyl alcohol are not quite clear.

Adolph and Rabinovich (Journ. Amer. Chem. Soc., *64*, 954, 1922) consider that of all the factors the following may have a deciding influence on changes in viscosity with concentration: (1) Influence of the viscosity of the solution on the internal friction of solution; (2) Changes in hydration of ions in dilute solutions; (3) Formation of complex ions and molecules—specially well pronounced in moderately and highly concentrated solutions—will increase viscosity if the volume of the complex ion is larger than the sum of the volumes of the simple ions composing it and decrease the viscosity in the opposite case; (4) Depolymerisation of the solvent on addition of electrolytes and depolymerisation of the solute by the solvent and (5) Influence of electric field due to ions.

The present results seem to support the assumption of Jones and Veazey (Jour. Amer. Chem. Soc., *37*, 405, 1906) about the specific effect of cation in lowering the viscosity with an increase of the concentration of the solution, for if the negative viscosity is as a result of the specific effect of the anion, all the chlorides, nitrates and iodides should have lowered the viscosity within a certain range of

concentration in the case of aqueous solutions. The non-observance of negative viscosity with nitrates and iodides in methyl, ethyl and n-propyl alcohols might be due to lower dielectric constant of the solvent. These results show that the tendency for negative viscosity decreases with the dielectric constant of the solvent. This effect of relatively low dielectric constant on negative viscosity appears somewhat like the effect of relatively high temperature on the same, for as observed by Sprung (Ann. Phys. Chem., *1*, 159, 1876), negative viscosity effect becomes less marked with an increase of temperature and disappears at high temperatures [also see in this connection Getman (loc. cit.) and Joy and Wolfenden (loc cit.)]. According to Happart (reference from Landolt and Börnstein, 4th edition, p. 288) the volume changes on the addition of solute to solvent might be partly responsible for negative viscosity in certain cases.

From the results obtained by us it has been found that the percentage increase in viscosity for the same concentration of the solution is greater in ethyl alcohol than in methyl alcohol, while that in n-propyl alcohol is greater than either in the case of methyl or ethyl alcohols. These results thus support the view that the increase in viscosity with an increase in concentration of solution becomes more marked the lower the dielectric constant of the solvent.

(*b*) *Relation between equivalent conductivity and fluidity.*

It has hitherto been the general practice to discuss the relation between equivalent conductivity and fluidity ($1/\eta$) instead of equivalent conductivity (Λ_c) and viscosity itself. In Figs. 6 and 7 are

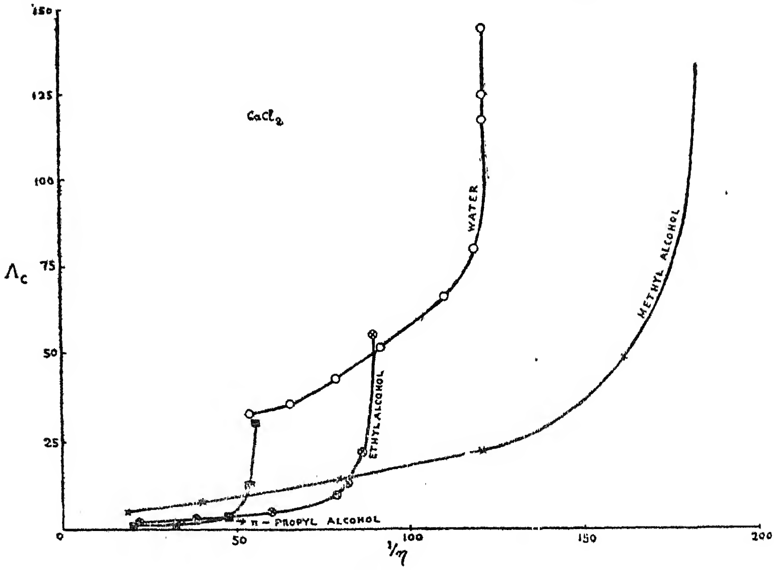

Fig. 6.

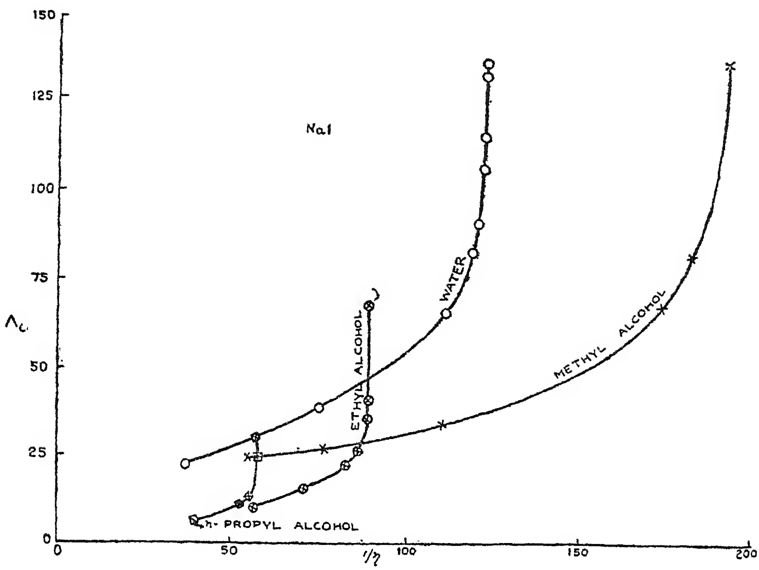

Fig. 7.

plotted the values of Λ_c [given in our previous paper (loc. cit.)] against $1/\eta_c$ for solutions of $CaCl_2$ and NaI respectively in different solvents. The nature of the curves in other cases, except those where negative viscosity is shown, is exactly similar. It will appear that for small decrease in fluidity of solution the equivalent conductivity decreases very rapidly for relatively dilute solutions, while in the concentrated solutions the decrease in the equivalent conductivity is much less than the decrease in the fluidity of the solution.

Walden (Z. physik. Chem., *55*, 207, 1906 ; *78*, 257, 1912 ; Z. f. Electrochemie, *26*, 67, 1920) has collected a large amount of data and come to the conclusion that the conductivity at infinite dilution of an electrolyte is inversely proportional to the viscosity of the solvent. It must be stated that only a rough parallelism between the viscosity of a solvent and the resistance it opposes to the passage of ions can be drawn from the results of Walden. From his data it becomes clear that in the majority of cases $\Lambda_o\eta_o$ only approximates to constancy in solvents whose dielectric constant is low ; directly one comes to solvents like water for which the dielectric constant is high, larger values of $\Lambda_o\eta_o$ are obtained. It thus appears that $\Lambda_o\eta_o$ is a function of the dielectric constant. According to Walden (loc. cit.) the factor $\Lambda_o\eta_o M^{1/2}$, where M is the molecular weight of the solute, is also constant for different solvents. In Table II are given the values of the above factors for NaCl, NaI and $NaNO_3$ in

different solvents, the value of Λ_o being that calculated from Lattey's (Phil. Mag., *6*, 258, 1928) equation.

TABLE II

		Water.	Methyl Alcohol.	Ethyl Alcohol.	n-Propyl Alcohol.
NaCl	Λ_o	143·5	99·36	44·55	27·19
	$\eta_o \times 10^2$	0·8007	0·5269	1·103	1·702
	$\Lambda_o\eta_o$	1·149	0·5235	0·4914	0·4627
	$\Lambda_o\eta_o M^{1/2}$	67·28	30·63	28·75	27·07
	$\Lambda_o\eta_o/D$	0·01497	0·01779	0·01997	0·02207
NaI	Λ_o	138·4	109·2	49·72	31·21
	$\eta_o \times 10^2$	0·8007	0·5206	1·060	1·710
	$\Lambda_o\eta_o$	1·109	0·5684	0·5271	0·5337
	$\Lambda_o\eta_o M^{1/2}$	166·3	85·27	79·07	80·05
	$\Lambda_o\eta_o/D$	0·01444	0·01932	0·02142	0·02537
$NaNO_3$	Λ_o	144·0	109·6	49·65	31·09
	$\eta_o \times 10^2$	0·8007	0·5206	1·060	1·670
	$\Lambda_o\eta_o$	1·153	0·5707	0·5262	0·5192
	$\Lambda_o\eta_o M^{1/2}$	98·02	48·51	44·73	44·13
	$\Lambda_o\eta_o/D$	0·01502	0·01939	0·02138	0·02468

It will appear that the two sets of values are quite different for water and methyl alcohol. It will thus be apparent that knowing the value of Λ_o for a salt in one solvent, it will not be possible to get even a rough value of Λ_o for the same salt in another solvent whose chemical nature is different. However the agreement of the value in different alcohols is fairly close.

Table II also contains the values of the factor $\Lambda_o\eta_o/D$, where D is the dielectric constant of the solvent. It will be seen that the value of this factor is very nearly the same in water as well as in methyl alcohol, the difference being less than 25% in this case, while it is about 100% in the case of values of the factor $\Lambda_o\eta_o$. It will also be seen that the value of the factor $\Lambda_o\eta_o/D$ rises continuously as the dielectric constant decreases. The value of Λ_o for NaCl in n-propyl alcohol calculated from the value of the factor for water comes to 18·51. The actual value calculated from Lattey's equation is 27·19. The calculated value of Λ_o for NaCl in n-propyl alcohol is

lower than the actual value which will be observed in that solvent for the same salt probably because of the fact that the solvation of ions in n-propyl alcohol is less than in water. If the solvation of ions in n-propyl alcohol is less than in water, other things being taken into consideration, the smaller effective radii of ions in the former solvent will give higher value of Λ_o than the value of Λ_o calculated from the data for water on the assumption that the effective ionic radius is the same in both the solvents.

Grüneisen (loc. cit.) has observed that the expression $[(\eta_c/\eta_o)-1]/m = A\alpha + B\ (1-\alpha) + Cm$, where A, B and C are constants, α is the degree of dissociation, m is the concentration in gram-equivalents and η_c and η_o are the viscosities of solution and solvent respectively, fitted the experimental observations upto concentration several times normal. On applying his expression to the present results, it was not found to be valid at all.

Bousfield and Lowry (Phil. Trans., *204*, 289, 1903) suggested that the measured activities should be multiplied by the relative viscosity in order to account for the effect of fluidity on the mobility of the ions. The values of $\Lambda_c\ \eta_c/\eta_o$ for some of the salts in different solvents have also been calculated. It is found that in all the cases in water there occurs a minimum in the corrected conductivity at higher concentrations. In the case of alcohols the minimum in the corrected Λ_c also occurs at higher concentrations in those cases where the solubility is large ; in cases where the solubility is small the minimum is not observed. According to Kraus (Jour. Amer. Chem. Soc., *36*, 35, 1914) in cases of large negative viscosity effect the corrected value of Λ_c decreases in a regular way with increasing concentration. His observation is completely supported by all the cases of negative viscosity mentioned in this paper. Two explanations have been advanced for the occurrence of the minimum in the corrected values of Λ_c :—

(1) According to Franklin (Journ. Phys. Chem., *15*, 683, 1911) who investigated KI in liquid sulphur dioxide at 0°C, there occurs first a minimum point and then a maximum point in the Λ_c, C curve. Walden (Bull. Akad. Sci. Petersb., 1083, 1913) has stated that for any salt there exists a relationship between the position of minimum and the dielectric constant of the solvent. The causes of the minimum at higher concentration in the corrected Λ_c values might be similar to those of minimum in the value of Λ_c (experimental) observed in some non-aqueous solutions (Franklin, loc. cit.).

(2) According to Washburn (Journ. Amer. Chem. Soc., *33*, 1463, 1911) Λ_c has been over corrected and that it should be multiplied by the mth power of relative viscosity, where m is less than 1

and varies from ion to ion. Rabinovich (Z. physik. Chem., *99*, 338, 417, 1921) also considers that $\Lambda_c\ \eta_c/\eta_0$ figures are over corrected. It should however, be stated that the over correction does not wholly explain the facts.

It has also been found from our results that the viscosity corrected values of α (degree of dissociation) are in some cases higher in concentrated solutions than in dilute ones. This is certainly against all the known facts of physical chemistry.

It is difficult to say how much reliance should be placed on these corrections of viscosity. In concentrated solutions, where alone viscosity effects are large, there also exist undissociated molecules besides the ions. These three will be present in varying proportions and will presumably exert each its own individual effect on the viscosity of the solution. Moreover the mobilities of the ions may be differently affected by each of the three factors.

SUMMARY.

Measurements of viscosity of chlorides, nitrates and iodides of solutions of alkali metals and alkaline earths over a large range of concentration have been made using water and methyl, ethyl and n-propyl alcohols as solvents.

Chlorides, nitrates and iodides of potassium and ammonium in aqueous solutions show negative viscosity within a certain range of concentration; in methyl and ethyl alcohols KCl and NH_4Cl alone show negative viscosity, while in n-propyl alcohol only a tendency for negative viscosity is marked in the case of KCl alone. In other cases the viscosity increases continuously with concentration, the increase being more marked in concentrated solutions. An equation connecting viscosity with concentration has been suggested. These results have been discussed from points of view advanced by various investigators.

A discussion of relation between conductance (results of simultaneous measurements of conductance given in a previous paper) and fluidity has also been made. It has been observed that for relatively dilute solutions a small decrease of fluidity is accompanied by a very rapid decrease of Λ_c, while in concentrated solutions the decrease in Λ_c is much less than the decrease in fluidity. The same behaviour is shown by all salts in different solvents where fluidity decreases regularly with an increase in concentration. Applicability of Walden's rule has been discussed.

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A STUDY OF THE CHEMICAL CHANGES DURING THE FORMATION AND GERMINATION OF THE RICE GRAIN

BY

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The paper consists of the following three parts :—

1. A study of the chemical changes which take place during the formation of the Rice Grain.
2. A study of the chemical changes which take place from the time of sowing to the complete exhaustion of the food material from the Rice Grain.
3. A study of the action of the Amylohydrolytic Enzyme during the germination of Rice Grain.

The three problems were originally studied quite independently of each other but as they are very closely allied they have been included in one paper. Each section, however, has its own introduction and has its own conclusions separately stated.

I

A STUDY OF THE CHEMICAL CHANGES WHICH TAKE PLACE DURING THE FORMATION OF RICE GRAIN

Introductory.

The object of this investigation was to study the changes taking place in the stem and the inflorescence of the rice plant with special reference to the translocation of different ingredients for the building up of the material of the grain. Shinkichi Susuki (1917) of Japan in his publication "The Growth of Rice Plant" and Sahasrabuddhe (1928) in his publication "Assimilation of Nutrients by the Rice plant" have given indication of the way in which translocation takes place during the formation of rice grain along with the study of the other parts of the rice plants. The present investigation goes into details but restricts itself to the study of the development of the grain from the time of flowering to the time of complete maturity of the grain.

Experimental.

For the purpose of the experiments, seeds of Ambemohor variety, were sown in nursery beds, and the plants were transplanted into a plot of 10 gunthas, at the Poona Agricultural College Farm, in the last week of July 1932 ; the crop received all normal treatment, and

came to the flowering stage by the second week of October. On the 21st of October about 300 plants in the same stage of development were marked and labelled. On this day the labelled plants had put forward the flowering stalk out of the sheath, *i.e.*, the Flag-leaf had come out, and the flowers were yet to be fertilised. The first lot was taken and analysed on that very day. The successive lots were analysed every fourth day. In all 10 lots were obtained and these covered a period of 40 days. Each lot was analysed for the following constituents, and separate analysis was carried on for the upper and lower half of the inflorescence and the portion of the stem just below it :—

(1) Moisture.
(2) Albuminoids.
(3) Ether Extract.
(4) Crude fibre.
(5) Soluble Carbohydrates (By difference).

Containing :—

(*a*) Dextrins.
(*b*) Dextrose.
(*c*) Sucrose.
(*d*) Starch.

The results have been calculated on oven-dry-basis. The following is a short description of the different lots in their successive stages of development :—

Stage 1 :—

The average length of the stem below the flowering stalk and the portion that could be easily pulled out of the rest of the stem was 5″. The flowers in the upper half of the inflorescence were fertilised, and the lower ones were about to do so. The flowering-stalk had completely come out of the sheath, and its average length was nearly 8″.

Stage 2 :—

The flowers in both the lower and the upper half of the inflorescence were fertilised, and the length of the flowering-stalk was 10·5″. The average length of the stem below the inflorescence—*i.e.*, the portion that could be easily pulled out of the rest of the stem—was 11·4″.

Stage 3 :—

The formation of the grain had just started in the upper half of the inflorescence. The lower half of the inflorescence was yet to

start the formation of the grain. The average length of the flowering-stalk was 10·5″ and that of the stem below it was 11·5″.

Stage 4 :—

The upper portion of the upper half of the inflorescence had almost completed the formation of the grain and the lower half of the inflorescence was in the milk stage. The length of the flowering-stalk was 10·5″ and that of the stem below it was 11·5″.

Stage 5 :—

Grain formation was complete in the upper half. The lower half was still in the milk stage. The average length of the flowering-stalk was 11·5″ and that of the stem below it was 12″.

Stage 6 :—

There was complete grain formation in the whole of the inflorescence. Nearly the whole of the upper half had assumed a yellow colour. A little drying of the inflorescence had started at the upper end. The average length of the flowering-stalk was 11·5″ and that of the portion of the stem below it was 12·5″.

Stage 7 :—

Nearly the whole inflorescence had started drying and the upper half had nearly completely dried. The lower portions of the inflorescence were still green. The average length of the inflorescence was 11·5″ and that of the stem below it was 12·5″.

Stage 8 :—

Nearly the whole inflorescence had dried except the lower one-fourth portion and the general colour of the inflorescence was brownish-yellow. The average length of the flowering-stalk was 11·5″ and that of the stem below it was 12·5″.

Stage 9 :—

There was a general deepening of the colour and the whole crop had turned yellow. It was nearly ready for harvest.

Stage 10 :—

The crop was ready for harvest and was completely dried up. The leaves had become brittle though the stems in general were still a little green.

It will thus be seen that the complete formation of the grain from the time of flowering to the harvest of the crop covered a period of about 40 days. The crop was harvested in the last week of November 1932. It is interesting to note at this stage that in the case of the rice crop the development of the grain and the fertilisation of flowers starts from the topmost portion so that the upper portions are in a

more advanced stage of development than the lower ones. It indirectly means that all the food material that is translocated from the stems and the leaves first goes to the upper portions and then to the lower ones. As has been said previously, the upper and the lower half of the inflorescence and the portion of the stem just below it were analysed separately every fourth day and the results are calculated and expressed on oven-dry-basis. The following pages give a full account of the changes taking place in the different constituents of the rice plant during its successive stages of development.

Analytical Results :—

Table No. 1 gives figures for the portion of the stem just below the inflorescence while tables Nos. 2 and 3 give figures for the lower half and the upper half of the inflorescence respectively.

TABLE I.

Analysis of the portion of the stem just below the inflorescence.

Excepting moisture all the figures are on oven-dry-basis.

Stage.	Moisture.	Ash.	Crude Fibre.	Albuminoids.	Ether Extract.	Soluble Carbo-hydrates.	Reducing sugar.	Sucrose.	Dextrins.	Starch.
	←				Per cent					→
1	83·54	2·10	32·60	7·15	2·60	55·55	5·72	3·95	1·53	28·13
2	80·30	2·12	46·08	7·61	1·90	42·28	7·61	1·96	1·40	27·00
3	80·92	2·39	44·66	3·72	1·91	47·30	5·55	3·69	0·37	25·23
4	82·35	2·43	40·64	4·35	2·67	49·93	5·09	3·96	0·28	23·73
5	85·06	2·88	38·36	4·32	1·40	53·89	5·47	2·89	...	22·S0
6	85·06	2·31	36·30	4·14	1·78	55·46	3·01	3·84	0·42	21·59
7	83·64	3·02	41·66	4·64	2·80	47·87	3·02	1·55	...	21·53
8	86·44	2·73	44·30	4·00	2·00	46·96	3·31	1·54	0·48	20·30
9	87·35	3·57	42·66	2·82	1·75	49·18	3·32	1·12	0·54	18·06
10	83·86	2·55	40·62	3·00	1·45	52·37	2·47	0·76	0·47	16·86

TABLE II.

Analysis of the lower half of the inflorescence.

Excepting moisture all the figures are on oven-dry-basis.

Stage.	Moisture.	Ash.	Crude Fibre.	Albuminoids.	Ether Extract.	Soluble Carbo-hydrates.	Reducing Sugar.	Sucrose.	Dextrins.	Starch.
	←				Per cent					→
1	66·76	18·07	42·40	8·49	1·10	29·93	1·18	Nil	1·89	23·48
2	58·12	16·42	40·00	10·58	1·44	31·54	2·18	Nil	0·95	26·88
3	56·71	15·31	43·60	7·29	1·67	32·11	5·19	Nil	0·92	31·35
4	55·33	8·40	25·92	9·11	2·33	54·22	2·01	Nil	0·39	34·22
5	47·46	9·79	21·85	9·50	2·92	55·92	2·44	Nil	0·11	35·85
6	44·50	9·50	18·97	10·61	2·92	57·98	1·35	0·11	0·11	37·64
7	42·42	10·58	15·50	10·45	2·97	60·50	1·18	0·09	0·49	38·64
8	39·24	10·15	15·15	11·40	2·90	60·38	1·05	0·07	0·47	47·03
9	35·44	10·58	12·86	11·93	2·92	61·69	0·99	0·06	0·46	47·05
10	22·73	10·10	12·25	10·26	1·74	65·64	0·72	0·09	0·26	57·47

TABLE III.

Analysis of the upper half of the inflorescence.

Excepting moisture all the figures are on oven-dry-basis.

Stage.	Moisture.	Ash.	Crude Fibre.	Albuminoids.	Ether Extract.	Soluble Carbo-hydrates.	Reducing Sugar.	Sucrose.	Dextrins.	Starch.
	←				Per cent					→
1	60·05	19·55	39·76	15·73	6·29	18·67	2·04	Nil	0·87	16·43
2	61·30	20·45	38·84	9·45	2·00	29·16	2·77	Nil	1·31	18·62
3	56·71	13·47	28·04	10·76	2·33	45·38	5·93	Nil	0·56	32·45
4	46·68	9·72	25·48	10·11	2·90	51·77	2·41	Nil	0·19	37·64
5	37·43	11·48	20·17	10·29	3·10	54·94	2·19	Nil	0·12	41·77
6	32·50	14·51	19·17	8·93	2·23	55·14	0·74	0·38	0·12	47·03
7	28·54	15·01	12·15	9·40	3·06	60·36	0·70	0·39	0·53	47·03
8	27·23	13·05	12·01	8·93	2·73	63·27	0·61	0·41	0·63	48·34
9	27·31	10·40	12·93	9·43	2·77	64·45	0·61	0·26	0·82	50·22
10	15·65	10·31	10·68	9·43	1·51	68·05	0·53	0·25	0·49	58·82

Conclusions :—

1. The percentage of moisture remains nearly constant in the portion of the stem just below the inflorescence, throughout the successive stages of development. In the case of the inflorescence, however, it will be seen that it continues to fall from the beginning to the end and this holds true both with the upper and lower half of the inflorescence. It is interesting to note, however, that the lower half of the inflorescence is rather richer in moisture than the upper one.

2. The percentage of ash on oven-dry-basis remains nearly constant, in the portion of the stem below the inflorescence the variation in the figures being very slight. In the inflorescence, it will be seen that the figures for ash are high but they also are nearly constant in the last two stages of development.

3. The percentage of crude fibre increases in the stem but goes down gradually in the inflorescence and this is due to the steady accumulation of other constituents in the maturing grain.

4. The albuminoids do not suffer much change in the percentage throughout the period of development of the grain.

5. The percentage for ether extract fluctuates during the successive stages of development of the grain but the range of variation is rather narrow both for the inflorescence and for the portion of the stem just below it. These variations are probably due to the presence of unequal quantities of colouring matter of the plant and sometimes due to fatty acids that are extracted by ether.

6. In the case of the portion of the stem just below the flowering-stalk the percentage figures for soluble carbohydrates have a fluctuating nature. In the case of the inflorescence, however, this is not the case. Thus for both the upper and the lower half of the inflorescence there is a steady rise in the percentage-figures, and the maximum is reached in both the cases by the tenth stage of development of the maturing-grain.

7. The portion of the stem just below the flowering-stalk is richer in reducing-sugars than the portion of the inflorescence throughout the period of development of the maturing-grain. The fall in the percentage of this constituent in this organ of the plant suggests that these reducing-sugars must be getting translocated from the stem to the inflorescence. Further the slow decrease in these reducing-sugars in the portion of the inflorescence after the fourth stage of development, appears to be probably due to their transformation into starch or some such higher carbohydrates.

8. It will be seen that as with reducing-sugars, so also with sucrose the portion of the stem just below the inflorescence is much

richer than both the portions of the inflorescence, and that it continues to be so from the beginning to the end. In the first five stages no traces of the sucrose are to be detected in the portion of the inflorescence and it appears to come there later from the portion of the stem which is very rich in that constituent.

9. The figures for dextrins have great tendency to fluctuate. This seems to be due perhaps to the fact that the dextrins are intermediate products during the formation of one carbohydrate from another.

10. The percentage of starch goes on increasing from beginning to end, both in the upper and the lower portions of the inflorescence, and that with this steady increase there is a corresponding decrease in the same in the portion of the stem just below the flowering-stalk. Thus a part of the starch of the stem must be getting translocated to the portion of the inflorescence just above it. This statement is supported by similar results obtained by Shinkichi Susuki (1917) who remarks as follows :—

"A large amount of starch disappears in the stem after the time of flowering, at which time the highest amount of starch is contained by these organs. It appears therefore that the stem of the rice-plant stores starch to furnish carbohydrates to the grain."

II

A CHEMICAL AND BIOCHEMICAL STUDY OF THE CHANGES WHICH TAKE PLACE FROM THE TIME OF SOWING TO THE COMPLETE EXHAUSTION OF THE FOOD MATERIAL FROM THE SEED

Introduction.

The object of this investigation was to study the changes which are produced in the constituents, especially the changes in the carbohydrates, of the rice seed from the time it is sown to the time it is completely depleted of its food constituents. The period required for complete exhaustion covered 20 days. Since starch is the most important constituent of rice, investigation was concentrated chiefly on the changes produced in what are ordinarily called "soluble carbohydrates" or "digestible carbohydrates" and the study of the changes in the other constituents was incidental.

Chemical changes in the constituents

Several investigators have worked on the chemical changes taking place during the germination of oil seeds. H. T. Brown and G. H. Morris (1890) have done much work on the germination of barley and grass seeds. The present investigation is restricted only to the

rice seed, and deals with the changes which take place during a period of twenty days in which all the removable material is exhausted. This study does not concern itself with the changes taking place in the plumule or the radicle.

Experimental.

The seeds of the previous year's harvest were produced and were sown in medium black soil obtained from the College farm by the middle of June. The germination was carried on in dishes which were 2 inches deep and 9 inches in diameter. Each dish was sown with 25 grams of the seed. On the day of the sowing the dishes received 300 cc. of tap water and on subsequent days they received 100 cc. of the same per day. Every precaution with regard to uniform sowing, etc., was taken and the seeds were given suitable conditions for germination.

The germination was almost complete by the 4th day and on this day the average length of the radicle was 2·54 cms. and that of the plumule was nearly 1·5 cms. By complete germination is meant that stage of the plant development at which the new seedlings are capable of nourishing themselves with the food-material that is present in the soil, or with the food-material that they can manufacture from the air by the help of the Chlorophyll, even in the absence of any such supply in the seeds themselves. Thus on the 4th day the seedlings were in such a stage of development that they could have had an independent existence.

As already referred to above the experiment covered a period of 20 days from the time of sowing and in all five lots were made each of which was analysed for the different constituents every fourth day. Since the changes taking place in the seeds irrespective of those in the shoots and the roots were to be studied, the seeds of each of the above five lots were cleaned of all the adhering dirt and the portions of roots and shoots were then analysed for the following constituents :—

1. Moisture, 2. Ash, 3. Albuminoids, 4. Woody fibre, 5. Ether extract, and 6. Soluble Carbohydrates ;

the soluble carbohydrates were determined both by difference and also separately and they comprise the following :—

1 Dextrose, 2. Sucrose, 3. Dextrins, and 4. Starch.

Exactly 100 seeds were analysed for these different constituents and the percentages on oven-dry-basis as well as the actual quantities of each in 100 seeds were worked up subsequently.

TABLE IV.

Quantities of the various constituents present in 100 seeds of rice at various stages during germination.

Stage.	Dry weight.	Ash.	Crude Fibre.	Albuminoids.	Ether Extract.	Soluble Carbo-hydrates.	Starch.	Dextrose.	Sucrose.	Dextrins.	Total of four previous columns.
	←					Grammes					→
Before sowing...	1·43	0·09	0·17	0·10	0·03	1·02	0·90	0·00	0·01	0·004	0·92
4th day ...	1·42	...	...	...	0·04	0·93	0·69	0·03	0·00	Nil	0·73
8th day ...	0·74	0·08	0·12	0·03	0·04	0·44	0·25	0·47	0·00	Nil	0·30
12th day ...	0·48	0·08	0·13	0·03	0·04	0·17	0·07	0·01	Nil	Nil	0·08
16th day ...	0·45	0·08	0·13	0·02	0·03	0·17	0·04	0·01	Ni	Nil	0·05
20th day ...	0·36	0·07	0·13	0·01	0·01	0·12	Traces	Nil	Nil	Nil	Nil

General conclusions :—

In general the following conclusions can be drawn from the figures for the various constituents at different stages from the time of sowing to the exhaustion of plant food material—a period which extends over 20 days.

When the rice seed is sown it begins to absorb water rapidly and keeps up a high percentage of water throughout the period of 20 days.

The dry matter of the seeds naturally lost at every stage until at last a small quantity is left at the end of 20 days.

Taking the individual constituents we find crude fibre and ash are utilised only to a small extent.

Albuminoids are utilised to the extent of 90 per cent. of the original in 20 days.

The ether extract increases for some time due to formation of fatty acids produced during the decomposition of carbohydrates and albuminoids.

The soluble carbohydrates are first turned into dextrose and are then finally utilised by the growing parts of the new plant. It is hence that dextrose which is not present originally in the seed, makes its appearance, increases for some time and then disappears completely.

III

AMYLOHYDROLYTIC ENZYME

It is now a well-known fact that during the germination of seed, enzymes act as prominent agents in decomposing complex compounds into simpler ones. It is therefore natural to expect that enzymes must play an important part in splitting complex compounds during the germination of rice seed. In the case of the present investigation our study was restricted to the presence of an amylohydrolytic enzyme, as the most important compound to be split up, was the starch in the rice seed. In this study the amount of reducing sugars produced was taken as the measure of the activity of the enzyme.

Experimental.

Rice seeds were sown in the soil and natural conditions as regards moisture, uniform sowing, etc., were given to the seeds. On the 4th day plumules had an average length of 1·25 cm. and the radicles were nearly 1 cm. in length. These germinated seeds were completely freed from all the adhering soil and from plumules and radicles. 30 grms. of the seed was shaken in a bottle for 5 hours in 100 cc. of distilled water with the help of a hot air engine and kept standing for 24 hours. To prevent fermentative and other changes

toluene was added to the water used for extraction. Action of this extract was tried on ungelatinised and gelatinised starch. For comparison the action of diastase (Merk's) extract was tried. Six lots of flasks with duplicates were prepared as follows :—

1. Blank, extract of germinated seeds,
2. Blank, extract of 0·5 per cent. diastase,
3. Ungelatinised starch plus extract of germinated seeds,
4. Ungelatinised starch plus extract of 0·5 per cent. diastase,
5. Gelatinised starch plus extract of germinated seeds,
6. Gelatinised starch plus extract of 0·5 per cent. diastase.

The extract in each case was 20 cc. and the quantity of starch taken was 0·25 grms. Where gelatinised starch was used it was prepared by warming 0·25 grms. of prepared purified rice starch with a small quantity of water on a sand bath. To all the flasks toluene was added to prevent fermentation and other actions. All the flasks were kept at 26°C to 27°C. The action was allowed to go on for 24 hours. At the end of this period the action was checked by the addition of a few drops of strong alkali and by subsequently boiling on a sand bath for a few minutes. The volumes in the flasks were made up to 100 cc. and filtered through dry filter paper. The filtrates were titrated against Benedict's solution. The activity of the enzyme is expressed in terms of milligrammes of dextrose formed. The following are the results obtained in the above trials.

TABLE V.

Milligrammes of dextrose produced in 24 hours from 0·25 grms. rice starch.

Description of flask.	Dextrose produced.	
	A.	B. (Duplicate).
	Milligrammes.	Milligrammes.
1. Blank—containing extract of germinating seed.	44·54	44·54
2. Blank—containing extract of 0·5 grms. diastase.	Nil.	Nil.
3. Ungelatinised starch 0·25 grms. plus extract of germinated seed.	68·7	69·5
4. Ungelatinised starch plus extract of 0·5 grms. diastase.	Traces.	Traces.
5. Gelatinised starch plus extract of germinated seed.	302·5	307·6
6. Gelatinised starch plus extract of 0·5 grms. diastase.	222·2	222·2

Conclusions.

These trials distinctly show that there is an enzymic action on starch produced by the extract of germinating rice seed. The extract itself contains some starch which is changed into dextrose. The enzyme acts on starch added to the extract. Its action is far more active on gelatinised starch than on ungelatinised starch. When compared with 0·5 per cent. extract of diastase its action is more vigorous than that of the diastase.

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CONDENSATION OF ACETONE-DI-CARBOXYLIC ACID WITH PHENOLS AND PHENOLIC ETHERS

PART II.

Formation of 3-Keto-4-methyl-7-methoxy-hydrindenylidene-acetic Acid.

BY

DATTATRAYA BALKRISHNA LIMAYE

AND

GOVIND RAMCHANDRA GOGATE

In part I of this series (Limaye and Bhave, Journal of the Indian Chemical Society, 1931, *8*, 137) it has been shown that the condensation product of anisole with acetone-di-carboxylic acid had the constitution of a β substituted glutaconic acid, the substitution of acetone-di-carboxylic acid residue in the phenyl ring taking place in the para position to the methoxy group. It was thought interesting to study the condensation when the para position in the phenolic ether is already occupied, and a typical case, that of paracresolmethylether, was chosen.

At room temperature a condensation product was obtained, from which three substances were isolated :—(*a*) The already known 6-methyl-coumaryl-4-acetic acid (Dey, Journal of the Chemical Society, 1915, *107*, 1636), (*b*) A monocarboxylic acid, M.P. 218°C (Dec.), and (*c*) A di-carboxylic acid, M.P. 169°C (Dec.). When the condensation was carried out at a low temperature (0 to 5°C) however, the products consisted mainly of the abovementioned dicarboxylic acid and a new acid, M.P. 252°C, forming a fourth product. It was soon discovered that all these above four products were interrelated. Thus the dicarboxylic acid was found to yield, by the action of concentrated sulphuric acid, the monocarboxylic acid, together with the 6-methyl-coumaryl-4-acetic acid. The acid melting at 252°C was also found to yield the monocarboxylic acid, when acted upon by concentrated sulphuric acid.

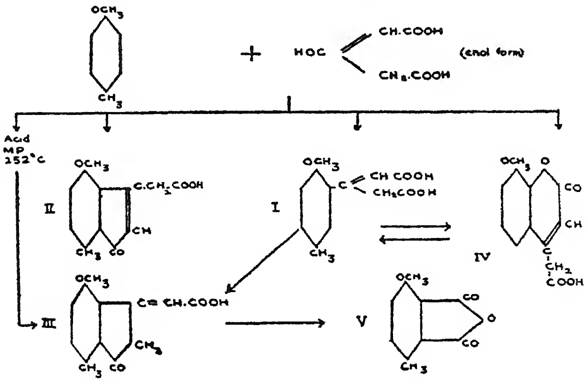
The dicarboxylic acid M.P. 169°C was proved to be a β substituted glutaconic acid by the preparation of its decarboxylation product, its hydroxy anhydride, a diester, a monoester, a semianilide and an anil (cf. Part I l.c.). The ortho position of the acetone-di-carbo-

xylic acid residue, with respect to the methoxy group in the phenol-ether, was evident from the transformation of the glutaconic acid into the 6-methyl-coumaryl--4-acetic acid, as well as from the constitution of its decarboxylation product, the demethylated product of which is known (Fries and Fickewirth, Berichte, 1908, *41*, 372). The phenol described by Fries and Fickewirth was prepared and on methylation gave a methyl ether identical with the decarboxylation product. Thus the glutaconic acid can finally be represented as β (2-methoxy-5-methyl-phenyl)-glutaconic acid (I). An additional proof of this constitution of the glutaconic acid is furnished by its synthesis directly from the 6-methyl-coumaryl-4-acetic acid, which will be reported in due course (cf. Limaye, Proceedings of the Indian Science Congress 1932, 226).

The constitution of the monocarboxylic acid M.P. 218°C was arrived at by the following considerations. Its equivalent and empirical formula indicated that one molecule of water had been eliminated in its formation from the dicarboxylic acid, by means of sulphuric acid. It was ketonic, in that it gave a semicarbazone and a phenylhydrazone. It melted with evolution of carbondioxide, yielding a neutral product which was also ketonic. These things go to show that only one of the carboxylic groups of the dicarboxylic acid has taken part in the elimination of water by sulphuric acid, apparently with one hydrogen atom of the benzene ring, thus forming a five membered ketonic ring. Thus the genetic relation of the monocarboxylic acid to the dicarboxylic acid fixed one of the positions of attachment of the five membered ketonic ring to the benzene ring, as ortho to the methoxy group. The second position of the attachment was proved by the oxidation of the monocarboxylic acid to a substituted phthalic anhydride (V) by means of nitric acid, thus indicating an indone (II) or a hydrindone (III) structure for itself according as one or the other of the carboxylic groups of the dicarboxylic acid, has taken part in the ring formation. The hydrindone structure was, however, established by the preparation of the isonitroso and benzylidene derivative of the ethylester of the monocarboxylic acid. The monocarboxylic acid can thus be finally represented as 3-keto-4-methyl-7-methoxy-hydrindenylidene-acetic acid (III).

The fourth product of the condensation, that is, the acid melting at 252°C, gave an ethylester M.P. 122°C, a semicarbazone, M.P. 272°C (Dec.) and a phenylhydrozone M.P. 205°C (Dec.). Its equivalent, empirical formula and its transformation into the hydrindenylidene-acetic acid by sulphuric acid, indicate that it is formed from two molecules of paracresomethylether and one molecule of acetone-di-carboxylic acid. Its exact constitution is under investigation.

The course of the condensation and the inter-relation of the resulting products can be represented as follows :—



EXPERIMENTAL

The condensation at room temperature (25 to 28°C).

To an acetone-di-carboxylic acid and sulphuric acid mixture, prepared from 25 gm. citric and 40 cc. sulphuric acid, (cf. Part I, l.c.) 10 gm. of paracresolmethylether were gradually added with shaking and the whole was left overnight at room temperature. The darkened semisolid mixture was poured into 150 cc. ice cold water. The solid that separated was taken on a filter, washed and dried. Yield 8 gm.

3-Keto-4-methyl-7-methoxy-hydrindenylidene-acetic acid. (III).

The above crude product of condensation was dissolved in 300 cc. of boiling alcohol, the solution filtered and allowed to cool, when silky long needles separated which on recrystallisation melted at 218°C (Dec.). Yield 0·8 gm.

Analysis :—

	Found C=67·17 ; H=5·11 per cent.		Equivalent =232·6
$C_{13}H_{12}O_4$	requires C=67·24 ; H=5·17	„ „	Equivalent =232 (monobasic)

The acid is soluble in glacial acetic acid and sparingly souble in alcohol. It is recovered unchanged from its solution in cold dilute alkalis ; but is changed into coloured products when boiled with concentrated caustic alkali solutions.

It can be prepared more conveniently from β (2-methoxy-5-methyl-phenyl)-glutaconic acid by the action of sulphuric acid.

6-Methyl-coumaryl-4-acetic acid, (IV).

On concentrating the alcoholic filtrate after the separation of the above acid (III) to about 50 cc. and cooling, most of the 6-methyl-coumaryl-4-acetic acid M.P. 180°C (Dec.) crystallised out. This was removed and the mother liquor was evaporated to dryness. The

residue on crystallising from boiling water gave, in the more soluble portion, 0·4 gm. of a dicarboxylic acid M.P. 169°C (Dec.) which is, however, obtained in better yield by effecting the condensation at low temperature.

Condensation at low temperature (0 to 5°C).

The mixture of acetone-di-carboxylic acid obtained from 200 gm. citric acid and 320 cc. sulphuric acid was cooled down in ice, 40 gm. of paracresolmethylether were added in small portions and the temperature maintained between 0 to 5°C for three hours. On pouring the reaction mixture on 1000 gm. of crushed ice, a sticky solid mass separated, which on allowing to stand overnight became hard and crystalline. It was filtered off, washed with water and dried. Yield 25 to 28 gm.

β (2-Methoxy-5-methyl-phenyl)-glutaconic acid. (I).

The above crude product of condensation at low temperature was dissolved in sodium carbonate solution. A small amount of the unchanged methylether was removed by passing steam through the solution ; it was then filtered and acidified with hydrochloric acid. The washed precipitate was treated with boiling glacial acetic acid, a small amount of an insoluble solid was filtered off and the filtrate poured in excess of cold water. The solid that separated was collected and crystallised from 10 per cent. boiling acetic acid, in colourless prisms, melting point 169°C (Dec.). Yield 22 to 24 gm.

Analysis :—

	Found	$C=62·3$; $H=5·5$ per cent.;	Equi. 125·1
$C_{13}H_{14}O_5$	requires	$C=62·4$; $H=5·6$ „ „	„ 125 (dibasic)

The dicarboxylic acid is readily soluble in alcohol and in glacial acetic acid, sparingly soluble in ether and insoluble in benzene.

On heating a mixture of 5 gm. of the glutaconic acid M.P. 169° with 15 cc. of concentrated sulphuric acid, for two hours at 50°C and pouring the resulting solution in 150 cc. of cold water a precipitate was obtained, which on crystallisation from 500 cc. of boiling alcohol, gave 1·5 gm. of an acid M.P. 218°C., identical with that obtained in the condensation at room temperature. From the mother liquor 2 gm. of 6-Methyl-Coumaryl-4-acetic acid were obtained.

Acid of Melting Point 252°C.

From the residue insoluble in acetic acid referred to above in the preparation of the glutaconic acid, on crystallisation from alcohol, an acid M.P. 252°C. was obtained. Yield 3 gm.

Analysis :—

	Found	$C=70·9$; $H=6·1$ per cent.;	Equi. 352
$C_{21}H_{22}O_5$	requires	$C = 71·2$; $H=6·2$ „ „	Equi. 354 (monobasic.)

The acid is insoluble in water and in benzene, sparingly soluble in ether and in alcohol. The sodium salt crystallises out in colourless leaflets from a solution of the acid in excess of caustic soda solution.

On heating 5 gm. of this acid with 25 cc. concentrated sulphuric acid at 70·80°C for one hour and pouring the solution in cold water a precipitate is obtained from which 3-keto-4-methyl-7-methoxy-hydrindenylidene-acetic acid, M.P. 218° could be recovered.

Anhydride of 3-methoxy-6-methoxy-orthophthalic acid. (*V*).

5 gm. of the mono-carboxylic acid M.P. 218°C described above were mixed with 50 cc. of dilute nitric acid. Sp. Gr. 1·2 and the mixture heated to boiling until the evolution of nitrous fumes ceased and the acid went into solution. The excess of nitric acid was removed on a boiling water-bath and the residual solution of about 10 cc. was allowed to crystallise. The crystals on re-crystallisation from absolute alcohol melted at 186°C. Yield 1 gm.

The substance is insoluble in cold water, sparingly soluble in benzene and soluble in glacial acetic acid.

Analysis :—

	Found	C=62·4 ;	H=4·1	per cent.
$C_{10}H_8O_4$	requires	C=62·5 ;	H=4·2	„ „

Equivalent by saponification was found to be 95·5 while a dibasic anhydride $C_{10}H_8O_4$ requires 96. It was not possible to isolate the free acid as it readily changes into the anhydride when set free from its sodium salt by dilute hydrochloric acid. The silver and barium salts were, however, readily obtained by precipitation. The anhydride nature of the oxidation product was further confirmed by the preparation of an acidic monoethyl ester $C_{12}H_{14}O_5$, M.P. 94°C and a neutral diethyl-ester.

The following table contains the products, derived from the two acids (I) and (III) and obtained by methods similar to those used in part I (l.c.) or by other known methods.

Substance	M.P. ° C.	Formula.	Analysis. Found	per cent.	Required	per cent.
	From β (2-methoxy-5-methyl-phenyl)-glutaric acid. (I).					
1. Anhydride	117	$C_{13}H_{12}O_4$	C=67·1 :	H=5·0	C=67·2 :	H=5·1
2. Diethyl ester	B.P. 207/5 mm.	$C_{17}H_{22}O_5$	C=66·5 :	H=7·1	C=66·7 :	H=7·2
3. Monoethyl ester	82	$C_{15}H_{18}O_5$	C=64·6 :	H=6·4	C=64·7 :	H=6·5
4. Semianilide	148	$C_{19}H_{19}O_4N$	C=69·9 :	H=5·8	C=70·1 :	H=5·9
5. Anil	225	$C_{19}H_{17}O_3N$	C=74·1 :	H=5·4	C=74·3 :	H=5·5
6. 2 - methoxy - 5 - methyl - isopropylenebenzene	B.P. 205	$C_{11}H_{14}O$	C=81·2 :	H=8·6	C=81·5 :	H=8·6
7. β (2 - methoxy - 5 - methyl - phenyl) - 2 : 6-dihydroxy-pyridine	200	$C_{13}H_{13}O_3N$	C=67·3 :	H=5·5	C=67·5 :	H=5·6
8. Dibenzoate of pyridine derivative (7)	134	$C_{27}H_{21}O_5N$	C=73·6 :	H=4·7	C=73·8 :	H=4·8
	From 3-keto-4-methyl-7-methoxy-hydrindenylidene-acetic acid. (III)					
9. Ethyl ester	158	$C_{15}H_{16}O_4$	C=69·1 :	H=6·1	C=69·2 :	H=6·2
10. Semicarbazone	252 (dec)	$C_{14}H_{15}O_4N_3$	C=58·2 :	H=5·3	C=58·1 :	H=5·2
			Equivalent	=288	Equivalent	=289
11. Phenylhydrazone	213 (dec)	$C_{19}H_{18}O_3N_3$	C=70·6 :	H=5·5	C=70·2 :	H=5·6
12. Semicarbazone of ethyl ester (9)	234 (dec)	$C_{16}H_{19}O_4N_3$	C=60·4 :	H=5·9	C=60·6 :	H=6·0
13. Isonitroso derivative of ethyl ester (9)	216 (dec)	$C_{13}H_{11}O_5N$	C=59·5 :	H=4·1	C=59·8 :	H=4·2
14. Benzylidene derivative of ethyl ester (9)	143	$C_{22}H_{20}O_4$	C=75·6 :	H=5·6	C=75·9 :	H=5·8
15. Decarboxylation product.	83	$C_{12}H_{12}O_2$	C=76·3 :	H=6·3	C=76·6 :	H=6·4

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LIGHT FILTERS FOR THE MERCURY ARC

BY

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Light filters for the isolation of the intense radiations from the mercury arc have been described from time to time by various investigators. A number of manufacturers have also devised coloured glasses or dyed gelatin films for the isolation of visible lines and the group of ultra-violet lines at the wave length 3650A. Some of these filters have a fair amount of transmission for the particular lines for which they are designed, yet their monochromatic quality is not satisfactory. When used with such instruments as a polarimeter, refractometer or an interferometer they introduce a certain amount of error in the measurements. The filters available at present for photochemical work in the ultra-violet region have a drawback, in that their transmission of the intense visible radiations from the arc is sometimes too great. These radiations even if they are not effective in producing a given photochemical change, they still cause considerable difficulty in the measurement of absorbed light energy. It, therefore, seemed necessary to survey the literature on the subject and to re-examine some of the existing filters. In the course of the work it was found that some of these filters after suitable modifications showed much improvement, particularly in respect to their monochromatic quality.

The work involved the examination of the absorption spectra of a large number of inorganic salts and organic substances. A Hilger Spekker spectrophotometer in conjunction with a small spectrograph was employed for this purpose. The extinction curves thus obtained furnished the transmission data for the ultra-violet and the violet filters. The data on the filters for the rest of the visible lines are only approximate, being obtained by comparison with some filters of known transmission.

In the tables given below are described a number of filters which are considered to be best for the isolation of various lines or group of lines. The percentage transmission of radiations in each case is also given. Remarks at the end of each table show the particular absorption qualities of the substances employed. Filters marked with an asterisk have been newly proposed.

TABLE I

Filters for the red line at λ 6907A

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)	Zeiss filters A and B combined.	35	....
(ii)*	Malachite green 0·54 gm. and cobalt sulphate hydrated 2·2 gm. dissolved in 70 cc. water. 4·0 cm. thick.	62	....
(iii)	Wratten filters No. 25 and 35 combined.	46	....

Remarks : (*ii*) The dye malachite green has a sharp cut off at 6300A. The green and the infrared region upto about 1μ are transmitted. The former of these is removed by cobalt sulphate and the latter by a 5 cm. thick cell containing water.

TABLE II

Filters for the yellow doublet at λλ 5770/5791

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)	Zeiss filter A.	55	Red 6907 35 p.c.
(ii)	Wratten filter No. 22.	70	Red 6907 and 6234 80 p.c.
(iii)	Corning filter, code No. 348, 3·5 mm.	75	Red lines and a trace of 5461.
(iv)	Potassium dichromate 2·5 gm. and copper sulphate hydrated 3·9 gm. dissolved in 70 cc. water ; 4·0 cm. thick.	29	....
(v)*	Eosin 0·03 gm., Auramine 0·09 gm. and nickel chloride hydrated 8·5 gm. dissolved in 100 cc. water ; 4·0 cm. thick.	36	....

Remarks : Nickel chloride or copper sulphate solutions could be used for absorbing the red lines transmitted by filters (*i*), (*ii*) and (*iii*), but the transmission of the yellow lines would be reduced by about 50 p.c.

TABLE III

Filters for the green line at λ 5461A

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)	Zeiss filter B.	80	Red lines more than 60 p.c.
(ii)	Wratten filter No. 77A.	50	Transmits red lines freely.
(iii)	Corning filter code No. 512, 9·0 mm., combined with code No. 351, 3·5 mm.	35	....
(iv)	Picric acid 0·4 gm., copper sulphate hydrated 3·5 gm. and didymium nitrate 15·0 gm. dissolved in 300 cc. water ; 2·0 cm. thick.	32	....
(v)*	Potassium chromate 0·07 gm., copper sulphate hydrated 3·9 gm. and didymium chloride 3·5 gm. with a few drops of sulphuric acid dissolved in 70 cc. water ; 4·0 cm. thick.	46	....
(vi)*	Chlorine gas 6 atm. pressure 4·0 cm. thick, with copper sulphate and didymium chloride solutions as above in a separate 4·0 cm. cell.	54	....

Remarks : (*i*), (*ii*) and (*iii*) : For the removal of the red lines a copper or a nickel solution may be employed.

(*iv*), (*v*) and (*vi*) : The yellow substances picric acid, potassium chromate and chlorine remove the blue, violet and the near ultra-violet portions of the spectrum. Copper sulphate removes the red and the middle ultra-violet, while the didymium salt removes the yellow lines.

TABLE IV

Filters for the group of blue lines at λλ 4358, 4347 and 4339A

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)	Zeiss filter C.	36	Violet lines 1 p.c. traces of yellow and green.
(ii)	Wratten filter No. 50.	14	Violet lines 0·4 p.c.
(iii)	Corning filter, Noviol A, 3 mm., and filter, code No. 585, 4 mm.	22	....
(iv)*	Chance blue glass No. 7, and a saturated solution of sodium nitrite 1·2 cm. thick.	31	Violet lines 1 p.c.
(v)*	Copper sulphate hydrated 0·5 gm., 36 cc. ammonia (0·88 sp. gr.) in 100 cc. water, 4·0 cm. thick, combined with sodium nitrite solution as above in a separate cell.	40	Violet lines 0·1 p.c.
(vi)*	Copper ammonium sulphate solution as above mixed with 0·004 gm. of Rhodamine B.	36	Violet lines 0·8 p.c.

Remarks : The violet lines transmitted by filters (*i*) and (*ii*) could be removed either by sodium nitrite or a 3 p.c. solution of quinine sulphate. The copper ammonium sulphate solution employed in filters (*v*) and (*vi*) has a sharp transmission of about 60 p.c. in the violet region. Rhodamine B has a weak absorption band near the extreme violet and helps to weaken the violet lines of the mercury arc.

TABLE V

Filters for the group of violet lines at λλ 4108, 4078 and 4047A

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)	Corning filter, code No. 597, 4 mm. with code No. 306, 3·5 mm.	6	....
(ii)*	Chance violet glass No. 8, and copper sulphate hydrate, 7·0 gm. in 100 cc. water, 1·0 cm. thick.	14	....
(iii)*	Cobalt acetate saturated, copper sulphate hydrated 3·5 gm., didymium chloride 6·0 gm. and quinine sulphate 0·05 gm. dissolved in 100 cc. water, 2·0 cm. thick.	18	Blue 4358 less than 0·1 p.c.

Remarks : In filter (*ii*) copper sulphate solution absorbs completely the red line 6907 transmitted by Chance glass. In filter (*iii*), in place of quinine sulphate solution, Schott and Gen glass GG2, 2 mm. thickness could be used for the absorption of 3650 group of ultra-violet lines.

TABLE VI

Filters for the group of lines at λλ 3663, 3655 and 3650A

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)	Wratten filter No. 18 A.	40	u.v. line 3341, 10 p.c.
(ii)	Corning filter, code No. 586, 9 mm.	38	u.v. line 3341, 10 p.c.
(iii)*	Chance u.v. glass 2 mm., combined with a solution containing 0·04 gm., cinnamic acid and 0·02 gm. quinoline yellow, in 100 cc. solution 4·0 cm. thickness.	52	Red line 6907 transmitted.
(iv)*	Chance u.v. glass 4 mm., with saturated cinnamic acid solution, 4·0 cm. thickness.	75	Red line 6907 and violet lines 0·2 p.c.
(v)*	Cobalt acetate 5·2 gm., quinoline yellow 0·02 gm. and saturated cinnamic acid solution, in 100 cc. water 4·0 cm. thickness.	44	Red and yellow lines transmitted, violet lines 1 p.c.

Remarks : In filters (*i*) and (*ii*) u.v. line 3341 could be removed by cinnamic acid solution. A dilute solution of copper sulphate would remove the red line transmitted by filters (*iii*), (*iv*) and (*v*). The dye quinoline yellow employed in filters (*iii*) and (*v*) has a sharp absorption band in the blue and the violet region. Didymium salt would remove the yellow lines transmitted by filter (*v*).

TABLE VII

Filter for the u.v. line at λ 3341A.

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)*	Para - Nitrosodimethylaniline 0·15 gm. in 1000 cc. water, 1·0 cm. thickness, combined with Chance u.v. glass 1 mm.	14	U.V. group of lines 3130 3 p.c.

TABLE VIII

Filters for the group of lines at λλ 3132, 3126A

No.	Description.	Transmission per cent.	Other lines transmitted.
(i)	Thin silver film deposited on quartz plate.	50	3023 line 5 p.c.
(ii)	Potassium chromate 0·097 gms. in 500 cc. water, 2·0 cm. thickness and Chance u.v. glass 1 mm.	35	3023 line 8 p.c. 3341 line 1·6 p.c.
(iii)*	Cobalt acetate saturated 2·0 cm. and potassium chromate as above.	31	3023 line 1·5 p.c. 3341 line 0·8 p.c.

Remarks : A sharp cut off for the 3023 line could be obtained by an aqueous solution of potassium hydrogen phthalate (0·2 molar 1 mm.). The intensity of 3341 line is considerably less than the 3130 group.

TABLE IX

Filter for the resonance line λ 2536A.

No.	Description.	Transmission per cent.	Other lines transmitted.
(i) *	Chlorine gas at 6 atm. pressure 4·0 cm. quartz cell and a solution of 49 gm. nickel sulphate and 14 gm. cobalt sulphate in 100 cc. water 2·0 cm. thickness.	25	Line 2482 18 p.c.

Remarks : A dilute aqueous solution of thiophene absorbs the 2482 line sharply. It was however found that sulphur is precipitated on long exposure.

From a general examination of the foregoing tables it would be seen that the filters described have fairly good transmission, while the degree of monochromatism available is perhaps the best obtainable. It is obvious that when a high purity of radiation is unnecessary, the filters could be used in smaller thicknesses, with a consequent gain in the intensity of transmitted radiations. It should be also noted that on account of the great intensity of the mercury radiations, large amount of energy is transmitted through the filters, even after the required radiation is considerably absorbed. This would be readily seen from table X, wherein are given a few approximate readings of the galvanometer deflections obtained, when light passing through a number of individual filters is falling on the face of a thermopile. (These observations were made with a standard apparatus for measuring the quantum efficiency of photochemical reactions.)

TABLE X.

Filter No. Table.	Wave-length trans-mitted.	Galv. defln.	Filter No. Table.	Wave-length trans-mitted.	Galv. defln.
(ii) I	6907A	41 cm.	(i) VI	3650A	102 cm.
(v) II	5759A	52 cm.	(ii) VIII	3130A	14 cm.
(v) III	5461A	239 cm.	(i) IX	2536 A	11 cm.
(v) IV	4358A	52 cm.			

1 cm. deflection corresponds to 15·6 ergs cm^2.

The light intensity during these observations was not controlled, the galvanometer deflections are therefore liable to be in error by 10-15 per cent.

Further information regarding some of the light filters mentioned in this paper, and others in general may be had from the following publications :

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CHLORALIDES OF α-HYDROXY CARBOXYLIC ACIDS

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Städeler obtained the first chloralide by the action of sulphuric acid upon chloral (*Annalen,* 1847, *61,* 104). Wallach many years afterwards established its constitution. He was then able to prepare it by heating together chloral and trichloro-lactic acid ($\beta\beta\beta$ trichloro-α-hydroxypropionic acid) and to obtain other chloralides from αhydroxy acids on the same lines (Annalen, 1875, *193,* 1);

$$CCl_3\text{-}CHO + \begin{array}{l} HO-C.H.R. \\ \quad\ \ | \\ HO-CO \end{array} = HO_2 + CCl_3\,CH \begin{array}{l} \diagup O-CHR \\ \qquad\quad\ | \\ \diagdown O-CO \end{array}$$

We carried out work on chloralides of α-hydroxy carboxylic acids, *viz.,* lactic, malic, mandelic, tartaric, citric and mucic acids some years ago* since when others have published on the subject. As we have not been able to resume the work we are putting on record such of our results as are still of interest.

The chloralides, being saturated ring compounds, often admit of cis-trans isomerism: the radicals, $-CCl_3$ and -R, may be situated on the same side of the ring or on the opposite sides. The work that has been published indicates that the chloralides have still to be studied with a view to stereoisomerism. The discrepancies in melting point, that are to be seen at present, must needs be examined: some of them may prove to be due to the presence of cis-trans isomers.

Wallach's method, which consists in heating the reacting substances in a sealed tube, sometimes gives poor yields. We found that better results are obtained when the reaction is carried out (using chloral hydrate) at room temperature in the presence of sulphuric acid, a method that has been also used by Böeseken (*Proc. K. Akad. Wetensch. Amsterdam,* 1927, *30,* 55) and Yorston (*Rec. trav. chim.* 1927, *46,* 711). With aliphatic acids the method usually

*The present work was submitted in the form of a thesis for the M.Sc. degree of the University of Bombay in 1923.

gives yields that are well over 80 per cent., with aromatic acids it is less satisfactory but with benzilic acid it fails.

The chloralides of *r*-mandelic, citric and mucic acids were prepared using sulphuric acid method alone. With *l*-lactic, *l*-malic and *d*-tartaric acids, on the other hand, both Wallach's and sulphuric acid methods were followed and the products compared. *l*-Lactic acid and *l*-malic acid produced identical chloralides in both methods, whereas in the case of *d*-tartaric acid, the two methods led to different dichloralides : Wallach's method gives a substance that is optically inactive and the other, one that is optically active. Hence the racemisation occurs when *d*-tartaric acid is heated together with chloral at 150°. The optically active chloride is converted into the optically inactive compound by heating it with sulphuric acid at 115°-120° : racemisation occurs also under these conditions.

EXPERIMENTAL

Lactic acid chloride. Both Wallach's and sulphuric acid methods were employed in condensing chloral with *l*-lactic acid : an identical lactic acid chloralide m.p. 45° was obtained. Wallach (*loc. cit.*) and Böeseken (*loc. cit.*) give m.p. 45°. (Found : Cl, 48·59. $C_5H_5O_3Cl_3$ requires Cl, 48·53 per cent.).

Malic acid chloralide. Starting with *l*-malic acid, we obtained the same chloralide by the two specified methods : m.p. 139°-140° ; Wallach (*loc. cit.*, 36) gave m.p. 139°-140°. We obtained from it the ethyl ester, by preparing the acid chloride and pouring that substance into ethyl alcohol : m.p. 44°. Wallach (*loc. cit.*) gave m.p. 45°-46° (Found : Cl, 36·5. $C_8H_9O_5Cl_3$ requires 36·54 per cent.). Patterson and McMillan (*J. C. S.* 1912, *101*, 794) obtained an ethyl ester by heating together chloral and ethyl malate at 130° : m.p. 55°. Racemisation does not occur in any of these methods.

d-Tartaric acid dichloralide. *d*-Tartaric acid (15 g.) and chloral hydrate (33 g.) were treated with concentrated sulphuric acid (50 cc.) and left overnight. The solid which separated was collected, washed and dried (25 g.). The dichloralide crystallised from acetic acid in fine needles, m.p. 160°, and was dextro-rotatory. Compare Böeseken (*loc. cit.*) and Yorston (*loc. cit.*) (Found : Cl, 51·87. $C_8H_4O_6Cl_6$ requires Cl, 52·06 per cent.).

r-Tartaric acid dichloralide. This substance was prepared in two ways.

(1) *d*-Tartaric acid (15 g.) and chloral (20 g.) were heated together in a sealed tube at 150°-160° for 8 hours. When the contents of the tube were treated with water a white solid was obtained (1 g.); it was dried and crystallised from benzene and next from chloroform ;

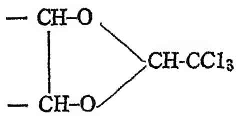
long needles m.p. 128°-130°, optically inactive. (Found : Cl, 52·05. $C_8H_4O_6Cl_6$ requires Cl, 52·07 per cent.).

(2) The above *d*-tartaric acid dichloralide (10 g.) was treated with sulphuric acid (200 cc.) at 115°-120°. The mixture was next filtered, using glass wool, and the filtrate when cold deposited crystals. The substance was collected, washed with water and crystallised from a mixture of acetic acid and water and next from chloroform, long needles, m.p. 128°-130°. This specimen was identified with the first by its appearance, by optical inactivity and by the melting point of a mixture.

That this substance is a true dichloralide of *r*-tartaric acid was further shown as follows. The substance was treated with a solution of potassium hydroxide so as to hydrolyse it ; next the solution was acidified using acetic acid and it slowly gave crystals of an acid potassium salt which was optically inactive. A neutral calcium salt was prepared which proved to be racemate. [Found : Ca, 15·41. $C_4H_4O_6Ca$, $4H_2O$ (mesotartrate) requires Ca, 16·53 per cent. $C_4H_4O_6Ca$, $4H_2O$ (racemate) requires Ca, 15·4 per cent.]

Citric acid chloralide. A mixture of citric acid (11 g.) and chloral hydrate (8 g.) was treated with sulphuric acid (20 cc.). On standing a solid separated which was filtered through glass wool, washed and dried (18 g.). The chloralide crystallises from acetic acid in tabular plates m.p. 161°. Böeseken (*loc. cit.*) gives 166°. It is less readily hydrolysed than the malic acid chloralide and can be titrated by alkali. (Found : equivalent, 160·3. $C_8H_7O_7Cl_3$ requires equivalent, 160·7). From solution in nitrobenzene it gives crystals that contain nitrobenzene. (Found : equivalent 191·1 $C_8H_7O_7Cl_3$, $\frac{1}{2}$ $C_6H_5NO_2$ requires equivalent 191·5). The acid chloride was prepared using the chloralide (5 g.) and phosphorus pentachloride (25 g.). After the removal of phosphorus oxychloride by distillation under reduced pressure the residue solidified : it crystallised from benzene in needles, m.p. 78°-79°, (Found : Cl, 49·31. $C_8H_5O_5Cl_5$ requires Cl, 49·47 per cent.). The methyl ester was prepared by boiling the chloralide with methyl alcohol in presence of a little sulphuric acid. It crystallised from petrol in six sided plates, m.p. 68°-69°, (Found : Cl, 30·40, $C_{10}H_{11}O_7Cl_3$ requires Cl, 30·45 per cent.). Edelenu and Zaharia [Chem. Zentr., 1895, (*ii*), 212] prepared a methyl ester using chloral, dimethyl citrate and sulphuric acid, m.p. 73°. The ethyl ester was prepared using the chloralide, ethyl alcohol and hydrochloric acid gas ; b.p. 215-225°/33 mm. (Found : Cl, 28·19. $C_{12}H_{15}O_7Cl_3$ requires Cl, 28·19 per cent.)

Mucic acid chloride. Mucic acid and chloral hydrate, in the proportion 1 : 3 molecules, were mixed with sulphuric acid as usual. After three days water was added : the precipitate was collected, washed, dried and crystallised from ether (yield almost theoretical) : plates, m.p. 200°-201°. (Found : Cl, 53·30. $C_{12}H_7O_8Cl_9$ requires Cl, 53·34 per cent.). The molecule contains two chloralide groups and also the group



Mandelic acid chloralide. *r*-Mandelic acid (5 g.), chloral-hydrate (5 g.) and sulphuric acid (15 cc.) were mixed. From the resulting solution a solid separated and more was obtained on adding ice to the mother liquor (6 g.). Crystallised from chloroform : small feathery crystals, m.p. 82°-83°. Wallach (*loc. cit.*, 38) gives m.p. 82°-83°. (Found : Cl, 37·82. $C_{10}H_7O_3Cl_3$ requires Cl, 37·80 per cent.).

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ACTION OF BROMINE ON *p*-METHOXY-SULPHONIC ACIDS

BY

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AND

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Meldrum and Shah (J. C. S., 1923, **123**, 1982) studied the action of bromine on *p*-hydroxy and *p*-methoxy-sulphonic acids and noted that the phenolic substance gives a bromo-sulphonic acid, the bromine atom being in the *ortho* position to the hydroxyl group, while the methyl ether gives the bromo-methoxy derivative, the bromine atom having replaced the sulphonic acid radicle.

In our work related to thiols derived from *o*-, *m*- and *p*-methoxy-toluenes and -benzoic acids (*ibid*., 1933, 1375) we prepared all isomeric methoxytoluene-sulphonic acids and a number of sulpho-methoxy-benzoic acids, *viz*., 4-and 5-sulpho 2-methoxybenzoic acids, 4-, 5- and 6-sulpho 3-methoxybenzoic acids and 2- and 3-sulpho 4-methoxybenzoic acids. When these acids were brominated it was found that only in the case of 3-methoxytoluene 6-sulphonic acid and 6-sulpho 3-methoxybenzoic acid, where the sulphonic acid group is in the *para* position to the methoxy group, the bromine atom displaced the sulphonic acid group producing 6-bromo 3-methoxytoluene, b.p. 236°-237°, and 6-bromo 3-methoxybenzoic acid, m.p. 162°, respectively, thus confirming the observations of Meldrum and Shah (*loc. cit.*). *m*-Tolyl methyl ether and *m*-methoxybenzoic acid gave identical products on bromination. Pschorr, Selle, Koch, Stoof and Treidel (Annalen, 1912, *391*, 23) describe 6-bromo 3-methoxybenzoic acid, m.p. 161°-162°.

EXPERIMENTAL

Bromination of 3-methoxytoluene 6-sulphonic acid (*6-Bromo-3-methoxytoluene*). For this purpose 3-methoxytoluene 6-sulphonic acid was first prepared : *m*-tolyl methyl ether (10 g.) was treated with 100 per cent. sulphuric acid (20 cc.) at 15° for 2 hours and the 3-methoxytoluene 6-sulphonic acid isolated in the form of its barium salt, rhombic plates. On treatment with potassium carbonate the barium salt yielded a potassium salt, square plates, containing one molecule of water (Found : K, 15·3 ; H_2O, 7·0. $C_8H_9O_4SK$, H_2O requires K, 15·1 ; H_2O, 7·0 per cent.). The latter, on trituration with phosphorus pentachloride and subsequent treatment with ammonia,

produced a syrupy 6-chlorosulphonyl 3-methoxytoluene and 6-sulphonamido 3-methoxytoluene, m.p. 130°. The salts, sulphonylchloride and sulphonamide are identical with those described by Haworth and Lapworth who prepared 3-methoxytoluene 6-sulphonic acid (*a*) from 6-nitro *m*-cresol (J. C. S., 1923, *123*, 2986) and (*b*) by sulphonating *m*-tolyl methyl ether with chlorosulphonic acid in carbon disulphide at 15° (*ibid.*, 1924, *125*, 1304).

The above methoxy toluene 6-sulphonic acid (4 g.) was dissolved in water (150 cc.) and a current of bromine passed with the aid of a water pump. Bromine was rapidly absorbed and a heavy oil separated when the theoretical amount of bromine was used up. The process was then stopped, the oil extracted with ether and distilled, b.p. 236°-237° (3 g.). An identical product was obtained on brominating *m*-tolyl methyl ether in acetic acid solution. (Found : Br, 39·76. C_8H_9OBr requires Br, 39 80 per cent.).

Bromination of 6-sulpho 3-methoxybenzoic acid (6-Bromo 3-methoxybenzoic acid). The acid potassium 6-sulpho 3-methoxybenzoate (4 g.), obtained from the above 3-methoxytoluene 6-sulphonic acid on oxidation with permanganate in the same way as described by Haworth and Lapworth (*loc. cit.* 1306), was dissolved in sulphuric acid (2 cc.) and water (90 cc.) and then treated with the vapour of bromine as shown above. The solution became slightly yellow coloured, when the required quantity of bromine was absorbed, and produced, on shaking, a crystalline flocculent mass which was collected, washed, pressed and crystallised from hot water (3 g.) 6 Bromo 3-methoxybenzoic acid separated in needles, m.p. 162°.

The same bromo-acid was produced when (*a*) 3-methoxy-benzoic acid was brominated in acetic acid solution and (*b*) 6-bromo 3-methoxytoluene, described above, was oxidised with alkaline permanganate. The admixture of the bromo-acids prepared by the three ways did not show any alteration in the melting point (Found : Equiv. 231·6 ; Br, 34·58. $C_8H_7O_3Br$ requires Equiv. 231·0 ; Br, 34·63 per cent.

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METHYLATION OF SOME SULPHO-AND NITRO-DERIVATIVES OF CRESOLS AND HYDROXY BENZOIC ACIDS

BY

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AND

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The methylation of phenols in aqueous (alkaline) solutions by means of methyl sulphate is quite common. Finding the method, however, inapplicable in the case of nitro derivatives of *m*-cresol Haworth and Lapworth (J. C. S., 1923, **123**, 2986) devised a special procedure for methylation, *viz.*, reaction with methylsulphate in xylene in presence of anhydrous potassium carbonate.

Hodgson and Nixon (*ibid.*, 1930, 2166) carried out a comparative quantitative investigation of the methylation of a number of substituted phenols and suggested that in the usual procedure methylation may be regarded as proceeding by initial attachment of methyl sulphate at the anionoid oxygen of the ionised phenol, but if the negative charge is not sufficiently localised (alternatively stated, if the oxygen electrons are insufficiently activated or mobile) no reaction will occur. In Haworth and Lapworth's procedure, on the other hand, ionisation is reduced to a minimum, so that the methylation must depend on the reaction between methylsulphate and the almost unionised potassium salt of the phenol at an incipient dipole, the formation of which will be enhanced by the nitro- and halogeno-substituents but repressed by methyl groups. These workers also noted the anomalous behaviour of 4-fluoro *2 : 6* dichlorophenol, 4-fluoro *2 : 6* dibromophenol and 4-fluoro *2 : 6* diiodophenol where methylation by one of the two methods leads to inconsistent results and of 5-nitro *o*-cresol where both methods fail.

In the course of work related to thiols derived from *o*, *m* and *p*-methoxytoluenes and -benzoic acids (Shah, Bhatt and Kanga, *ibid.*, 1933, 1375) as well as in subsequent work we studied the methylation of some sulpho- and nitro-derivatives of cresols and hydroxybenzoic acids extending over long periods of time and found that

(*i*) the usual procedure is applicable to the methylation of *o*-cresol 4-sulphonic acid, *p*-cresol 2-sulphonic acid, 4-

and 5-sulpho-salicylic acids and 4- and 5-sulpho *m*-hydroxy-benzoic acids, but does not hold good in the case of 3- and 5-nitro-*o*-cresols, 2-, 4- and 5-nitro *m*-cresols, 2-nitro *p*-cresol, 3- and 5-nitro-salicylic acids and 3-sulpho-salicylic acid, and

(*ii*) the special procedure of Haworth and Lapworth (*loc. cit.*) yields satisfactory results with 3- and 5-nitro *o*-cresols, 2-, 4- and 5-nitro *m*-cresols, 2-nitro *p*-cresol and 3-nitro-salicylic acid, but fails entirely in the case of 5-nitro-salicylic acid and 3-sulpho-salicylic acid.

The time required for complete methylation of the substance either by the usual procedure or by Haworth and Lapworth's method is given below :

Substance.	Time in hours.	
	Usual Procedure.	H. & L.'s method.
o-Cresol 4-sulphonic acid.	3	
p-Cresol 2-sulphonic acid.	2	
3-Nitro *o*-cresol.	..	12
5-Nitro *o*-cresol.	..	128
2-Nitro *m*-cresol.	..	16
4-Nitro *m*-cresol.	..	12
5-Nitro *m*-cresol.	..	10
2-Nitro *p*-cresol.	..	8
3-Sulpho-salicylic acid.	..	..
4-Sulpho-salicylic acid.	12	
5-Sulpho-salicylic acid.	16	
4-Sulpho *m*-hydroxy benzoic acid	6	
5-Sulpho *m*-hydroxy benzoic acid	6	
3-Nitro-salicylic acid.	..	18
5-Nitro-salicylic acid.	..	..

It is interesting to note that 3-sulpho-salicylic acid and 5-nitro-salicylic acid resist methylation by both the methods while the methylation of isomeric sulpho-salicylic acids is effected by the usual procedure and that of 3-nitro-salicylic acid by Haworth and Lapworth's method. In light of the proposed mechanism by Hodgson and Nixon (*loc. cit.*) these are anomalous cases demanding further investigation. It may be said, however, that the substances which

resist methylation by the usual procedure but get methylated by Haworth and Lapworth's method present instances of less steric hindrance than those in which even the latter method is not applicable.

EXPERIMENTAL

The methylation of substances other than 5-nitro *o*-cresol, *3*- and *5*-nitro-salicylic acids and *3*-sulpho-salicylic acid has been described in earlier papers (*vide* Meldrum and Shah, *ibid.*, 1923, *123*, 1992; Haworth and Lapworth, *loc. cit.*; Copisarow, *ibid.*, 1929, 252; Shah and Bhatt, *ibid.*, 1933, 1372 and Shah, Bhatt and Kanga, *loc. cit.*). In the experiments described below methylsulphate was added in moderate excess and methylation allowed to proceed for a maximum period of two months heating ten hours a day. For the success of the Haworth and Lapworth's method we found it essential to use dry xylene and freshly fused potassium carbonate, otherwise the results were unsatisfactory. The nitro-compound produced in the beginning, by interaction with potassium carbonate, a red colour which began to fade gradually as methylation proceeded further: the complete disappearance of the colour indicated that the reaction was at an end. With *3*-sulpho-salicylic acid, on the other hand, a portion of the reaction mixture was periodically removed and tested, in presence of water, with ferric chloride: the production of any violet coloration showed that the methylation was yet incomplete.

Methylation of 5-nitro o-cresol (5-Nitro 2-methoxytoluene). 5-Nitro *o*-cresol (15 g.) m.p. 86°, obtained by nitration of *o*-cresol and subsequent separation from *3*-nitro *o*-cresol by distillation with steam according to the method of Hofmann and Miller (Ber., 1881 *14*, 568), was dissolved in xylene, treated with anhydrous potassium carbonate and heated under reflux. Methylsulphate was added in small portions and the whole mixture well shaken at regular intervals during heating. After 128 hours, the flask was cooled and the mixture treated with water and a little sodium hydroxide solution. Xylene was then distilled off and *5*-nitro *2*-methoxytoluene obtained as a solid which when crystallised from alcohol separated in prismatic plates, m.p. 63° (14 g.). Simonsen and Nayak (*ibid.*, 1915, *107*, 828) give m.p. 62°-63°.

Methylation of 3-Nitro-salicylic acid (3-Nitro 2-methoxybenzoic acid). For this purpose *3*-nitro-salicylic acid, m.p. 128°-129°, obtained by nitration of salicylic acid and subsequent separation from *5*-nitro-salicylic acid, m.p. 228°, according to the method of Meldrum and Hirve (J. I. C. S., 1928, *5*, 95), was used. The *3*-nitro-acid (15 g.) was treated with xylene, potassium carbonate and methylsulphate as shown above. After 18 hours xylene was distilled off,

the solution carefully neutralised and then acidified with hydrochloric acid when *3*-nitro *2*-methoxybenzoic acid separated as a flocculent mass. On crystallisation from water it was obtained in wooly needles, m.p. 196°. The product was identical with that obtained from (*i*) *2*-methoxybenzoic acid on nitration (Simonsen and Rau, J. C. S., 1917, *111*, 220 ; Meldrum and Shah, J. I. C. S., 1931, 575) and (*ii*) *3*-nitro *o*-tolyl methyl ether on oxidation (Shah, Bhatt and Kanga, *loc. cit.*) : a conclusion arrived at by the mixed melting point test. When the three methods for the preparation of *3*-nitro *2*-methoxybenzoic acid are compared, the methylation of *3*-nitro-salicylic acid is found to give the best results.

Attempts to methylate *3*-sulpho-salicylic acid and *5*-nitro-salicylic acid were unsuccessful even though the period of methylation was extended to *two* months.

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THE REACTION BETWEEN ACETYLENE AND SULPHUR

BY

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The action of acetylene on sulphur has been studied by various workers. Meyer and Sandmeyer (Ber., 1883, 16, 2176) noted the formation of carbon, hydrogen sulphide, carbon disulphide and an oily substance giving an indophenin reaction. Capelle (Bull. Soc. Chim., 1908, 4, 150) and de Coninck (Bull. Acad. roy. Belg., 1908, 305) obtained, among the products of reaction, carbon disulphide, thiophten and a material with garlic-like smell but not thiophen. Peel and Robinson (J. C. S., 1928, 2068) represented the reaction yielding carbon disulphide and sulphuretted hydrogen together with carbon and small quantities of thiophen and thiophten, 500° being the optimum temperature of the reaction. Shepard, Henne and Midgley Jr. (J. A. C. S., 1934, 56, 1355) describe that acetylene reacts with iron pyrites at 350° giving a good yield of thiophen but with sulphur it produces thiophen or its homologues only in traces. We studied the reaction between acetylene and sulphur between 290° and 390° and found that the products contained thiophenol in addition to carbon disulphide, hydrogen sulphide, carbon and thiophten.

EXPERIMENTAL

The procedure followed by us consisted in passing purified acetylene gas through a vessel containing sulphur kept between 290° and 390°, collecting the materials distilling from the vessel and subsequently effecting their separation.

The reaction vessel was a distilling flask, the side tube of which was connected to a thick-walled vessel fitted with a vertical condenser. The latter in turn was attached to another vessel carrying a similar condenser. The reaction usually began at 290° with the formation of hydrogen sulphide and became rapid at 320° as noticed from the ignition of sulphur and copious evolution of yellow fumes. The condensible products collected in the form of a brown liquid in the thick-walled vessels while the uncondensible gases were passed through towers containing concentrated sodium hydroxide solution. In one experiment, sulphur (100 g.) yielded by interaction with acetylene the brown liquid (19 g.) and left a residue mainly consisting of carbon (13·0 g.).

The brown liquid on fractional distillation gave a portion (A) boiling between 50°-60° and another (B), above 70°. The distillation could not be carried out above 100° as the liquid showed signs of frothing and decomposition.

The portion (A), when further fractionated, gave two colourless liquids boiling at 48° and 49°-52° respectively. These fractions gave the indophenin reaction and were in all probability carbon disulphide contaminated with traces of thiophen.

The portion (B) was divided into *two* parts. The first part was treated with alcohol and the alcoholic solution allowed to react with mercuric chloride: a dark brown precipitate, m.p. 184°-185° (decomp.), was obtained. On analysis it was found to be a mercury salt of thiophenol. (Found: Hg, 47·5; S, 14·8. $C_{12}H_{10}S_2Hg$ requires Hg. 47·6; S, 15·3 per cent.). The mercury salt on decomposition with hydrochloric acid and subsequent extraction with benzene yielded a thick orange liquid with a garlic smell, b. p. 165°-168°. It reacted vigorously on skin, dissolved freely in alcohol and sodium hydroxide solution and was unaffected by water. Thiophenol gives similar reaction and boils at 169·5°.

The second part was treated with sodium hydroxide and the alkaline solution distilled with steam. The distillate when extracted with ether gave a dark yellow liquid, b.p. 210°-215° and an orange liquid, b.p. 232°. Both these fractions gave (*i*) the indophenin reaction and (*ii*) an identical picrate, golden yellow needles, m.p. 133°. Thiophten, according to Richter (1910), boils at 224°-226° and gives a picrate, golden yellow needles, m.p. 133°. Meyer and Jacobson (1920, Vol. II, Part 3) give for thiophten, b.p. 226°-228°. Peel and Robinson (*loc. cit.*) also describe a fraction, b. p. 210°-220°, giving the reaction of thiophten. The alkaline solution which was left behind during the steam distillation was acidified with hydrochloric acid and again distilled with steam. This distillate when extracted with benzene gave an orange liquid, b.p. 170°, with a garlic smell and was evidently thiophenol.

The sodium hydroxide solution which absorbed the gaseous products of the reaction was next distilled with steam. The distillate on extraction with ether left a small quantity of a liquid which gave reactions of thiophten. The residue was acidified with hydrochloric acid and subsequently distilled with steam. The ether extract of the distillate gave reactions of thiophenol.

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CONDENSATION OF 4-BROMO-PHENOL AND BROMO-CRESOLS WITH BENZOYL CHLORIDE AND *m*- AND *p*-NITRO-BENZOYL CHLORIDES

BY

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The methods, which are generally employed for the preparation of esters, are : (1) Action of acids on alcohols in the presence of dehydrating agents like concentrated sulphuric acid or dry hydrogen chloride. (2) Action of alkyl iodides on the silver salts of acids. (3) Action of acid-chlorides on alcohols.

Phenyl esters are generally prepared by the last method either by heating the two constituents together, or mixing them in the presence of caustic soda solution at room temperature. The esters, described in this paper, were prepared for confirming the constitutions of the bromo-esters obtained in a research on the bromination of compounds containing two aromatic nuclei.

EXPERIMENTAL

The general method, followed in this work, was heating together the acid-chloride and bromo-phenols in molecular proportions, till the evolution of hydrogen chloride ceased. The reaction mixture was diluted with water and the mass obtained was neutralised with caustic soda solution, washed and finally crystallised from a suitable solvent. In the case of 4-bromo-o-cresyl benzoate, the reaction is more easily carried out in the presence of 20 per cent. sodium hydroxide solution.

p-Bromo-phenol, 4-bromo-o-cresol, 4-bromo-m-cresol, 4 : 6 di-bromo-o-cresol, 2 : 6 dibromo-p-cresol and 2 : 3 : 6 tri-bromo-p-cresol were used and the new compounds obtained are shown in the table given below.

Name.	Formula.	Quantity of Phenol.	Time of heating.	Solvent and m.p.	Per cent. Bromine.	Per cent. Bromine required.	Shape.
4 - Bromo - o - cresyl benzoate	$C_{14}H_{11}O_2Br$	3 g.	Room Temperature	Alcohol, 63-64°	27·3	27·5	White shining needles.
2 : 6 di-bromo-p-cresyl benzoate	$C_{14}H_{10}O_2Br_2$	6 g.	4 hours	Acetone, 94-95°	43·1	43·2	Hexagonal transparent plates
2 : 3 : 6 tribromo-p-cresyl benzoate	$C_{14}H_9O_2Br_3$	3 g.	40 minutes	Acetone, 120°	53·5	53·5	Rhombic transparent plates
4 - Bromo-phenyl-m-nitro -benzoate	$C_{13}H_8O_4NBr$	8 g.	4 hours	Dilute acetone, 121-122°	24·5	24·8	White shining needles.
4-Bromo - phenyl p-nitro-benzoate	$C_{13}H_8O_4NBr$	8 g.	3 hours	Mixture of alcohol and acetone (1 : 1), 180-181°	24·6	24·8	White shining needles.
4-Bromo-o-cresyl p-nitro-benzoate	$C_{14}H_{10}O_4NBr$	5 g.	3 hours	Mixture of chloroform and acetone (1 : 1), 184°	23·6	23·8	White shining plates
4-Bromo-m-cresyl p-nitro benzoate	$C_{14}H_{10}O_4NBr$	5 g.	4 hours	Acetone, 144-145°	23·7	23·8	Shining plates
4 : 6 Di-bromo-o-cresyl p-nitro benzoate	$C_{14}H_9O_4NBr_2$	6 g.	3 hours	Acetone, 136-137°	38·3	38·6	Shining needles
2 : 6 Di-bromo p-cresyl p-nitro benzoate	$C_{14}H_9O_4NBr_2$	6 g.	5 hours	Mixture of acetone and Pet. ether (1 : 1), 141-142°	38·5	38·6	Shining plates
2 : 3 : 6 tri-bromo p-cresyl p-nitro benzoate	$C_{14}H_8O_4NBr_3$	8 g.	4 hours	Mixture of acetone and chloroform (1 : 1), softens at 156°, melts at 159-160°	48·4	48·6	Shining plates

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As a preliminary to a more complete investigation of the chemistry of dialkylaminobenzophenones, which have become readily available as the result of the work of Shah and Chaubal and the authors, the authors have studied several simple reactions of dimethyl aminobenzophenone and its derivatives.

The methiodide m.p. 188-190°, prepared by refluxing a mixture of the ketone with excess of methyl iodide in methyl alcohol, decomposes quantitatively on heating, preferably under reduced pressure to give the ketone and methyl iodide.

Bromination of the ketone gives 3-bromo-4-dimethyl-aminobenzophenone m.p. 78-80°.

Nitration with a mixture of conc. nitric acid in glacial acetic acid solution, or nitric acid conc. or dilute (1 : 1), gives the nitro compound m.p. 130° which is presumably 3 : 3′ : 5-trinitro-dimethyl aminobenzophenone. Meisenheimer, Budkewicz and Kananow (loc. cit.) nitrated dimethyl-aminobenzophenone with fuming nitric acid and obtained a tetranitro derivative, m.p. 175-175·5°, to which they ascribed the formula of a nitramine tetranitromethylamino-benzophenone, $NO_2-C_6H_4-CO\ \ C_6H_2(NO_2)_2-N-CH_3\ NO_2$ (NO_2 – NO_2 – N-MeNO_2 – NO_2 = 3 : 5 : 4 : 3′), one of the methyl groups being displaced by a nitro group.

Beckmann-transformation of p-dimethylaminobenzo-phenone-oxime.

Dimethylaminobenzophenone-oxime, best prepared by the alkali method, on being subjected to the Beckmann transformation, gave a compound m.p. 226-228°, which was definitely proved to be benzoyl-p-aminodimethyl-aniline $C_6H_5-CO-NH\ \ C_6H_4\ \ N(Me)_2$ by direct comparison with an authentic specimen.

The configuration of the oxime of an unsymmetrical ketone can be determined from the nature of the product of the Beckmann-transformation. According to Hantzsch, the hydroxyl group of the N – OH radical changes place with the aryl radical in the syn position. Meisenheimer (Ber., 1921, *54,* 3195, 3206 ; cf. also Brady and Bishop, J. C. S. 1925, *127,* 1357) has proved that Hantzsch's assumption about the transposition of groups in the syn positions is unwarranted and erroneous. According to him the Beckmann transformation occurs through the interchange of groups in the anti-position and must now be represented as follows :—

$$\begin{array}{lllll}
R-C-R' & \rightarrow & R-C-OH & \rightarrow & R-CO-NH\,R' \\
\quad\ \ \| & & \quad\ \ \| & & \\
OH-N & & R'-N & & \\
R-C-R' & \rightarrow & OH-C-R' & \rightarrow & R'-CO-NH-R \\
\quad\ \ \| & & \quad\quad\ \ \| & & \\
\quad\ \ N-OH & & \quad\quad\ \ N-R & &
\end{array}$$

In the present case, if $R = C_6H_5$, and $R' = C_6H_4\,N(Me)_2$, the final product would be either benzoyl-p-aminodimethyl aniline $C_6H_5-CO-NH-C_6H_4-N(Me)_2$, or dimethylaminobenzanilide $N(Me)_2\,C_6H_4CO.\,NH.\,C_6H_4$. The product actually obtained is benzoyl-p-aminodimethylaniline. Thus the oxime is shown to have the anti-configuration $C_6H_5-C-C_6H_4\,N(Me)_2$.

$$\begin{array}{c} \| \\ OH-N \end{array}$$

EXPERIMENTAL

Dimethylaminobenzophenone-methiodide.

An excess of methyl iodide (3 g.) was added to a solution of the ketone (0·5 g.) in methyl alcohol, and the mixture refluxed for about 4 hours. The pale yellow crystalline solid which separated on cooling was filtered off and then treated with cold benzene to remove unreacted ketone. The crude substance (0·5 g.) when crystallised from hot water to which a few drops of alcohol were added, gave colourless needles m.p. 188-190° (decomp.). Döbner (Annalen, 1881, 210, 269) who obtained it by the action of excess of methyl iodide on p-aminobenzophenone gives m.p. 181°.

Thermal decomposition of the methiodide.—0·1 g. of the foregoing methiodide was heated under 3 mm. pressure in a hard glass test tube immersed in an oil bath. The methiodide immediately after melting at 188-190°, decomposed with strong effervescence, which died out after a few seconds. The solution of the oily residue in hot petroleum ether gave on cooling crystals of dimethylaminobenzophenone.

3-Bromo-4-dimethylaminobenzophenone :—A chloroform solution of bromine (1·5 g.) was added to a solution of the ketone (2 g.) in chloroform. The oil left behind after evaporation of the chloroform was washed with a very dilute solution of sodium carbonate and then extracted with ether. The ethereal solution which was washed and dried, on evaporation deposited square plates, which on recrystallisation from rectified spirit gave crystals m.p. 78-80° (found : Br, 26·2 ; $C_{15}H_{14}\,ON\,Br$ requires Br, 26·3%).

3 : 3′ : 5 – Trinitro-dimethylaminobenzophenone :—*Dimethylaminobenzophenone* (1 g.) was dissolved in the minimum quantity of cold glacial acetic acid and excess of conc. nitric acid (10 cc.) added. The mixture on standing overnight deposited fine yellow needles (0·2 g.) which were washed with conc. nitric acid and then with water. The yellow needles when recrystallised from alcohol had m.p. 130° (Found : N, 15·5 ; $C_{15}H_{12}O_7N_4$ requires N, 15·6%). It is soluble in hot alcohol, cold chloroform and benzene. It is sparingly soluble in petroleum ether.

The filtrate from the above when diluted with water gave more of the nitro compound as a yellow crystalline solid, which on crystallisation from alcohol, gave yellow needles, which melted at 130° alone or admixed with the compound which separated directly from the nitration mixture.

An excess of conc. nitric acid was added directly to the ketone and then allowed to stand. The same nitro compound separated in tiny needles m.p. 129-130°.

Nitration with dilute nitric acid (1 : 1) also gives the same nitro-derivative.

Beckmann transformation of p-dimethylaminobenzophenone-oxime.

The oxime, which has been described before (Shah, Deshpande and Chaubal J., 1932, 645) is best prepared by the alkali method (cf. Lachmann, J. Am. Chem. Soc., 1925, *47*, 260). p-Dimethylamino-benzophenone (3 g.) was dissolved in alcohol (30 cc.) and to the solution were added hydroxylamine hydrochloride (1·5 g.) and potassium hydroxide (0·6 g.) dissolved in water (5 cc.). The mixture was refluxed for about 1 hour, and then poured into faintly acidified ice-cold water. The oxime separated as a colourless crystalline precipitate, which was filtered off, washed well with cold water and dried. The crude oxime (3 g.) was washed with cold benzene to remove unchanged ketone and finally crystallised from aqueous alcohol when it was obtained as colourless prisms m.p. 154-155°.

The oxime (0·2 g.) was dissolved in anhydrous ether (20 cc.) and phosphorous pentachloride (0·4 g.) added gradually. The mixture was refluxed for about 10 minutes after which the ether was distilled off. The residue was treated with water when a clear solution was obtained. On making the solution alkaline, a dirty white precipitate was obtained, which was filtered off, washed with water and cold alcohol and dried. The crude product (0·15 g.) had m.p. 193-223°. Two crystallisations from alcohol gave shining needles m.p. 226-228°. This compound appeared to be benzoyl-p-amino-dimethylaniline whose melting point is stated in literature to be 228°.

An authentic specimen of the substance was prepared by benzoylating p-amino-dimethylaniline obtained by the reduction of methyl orange. A comparison of the crystalline form, solubility and other properties of the two substances, together with a mixed melting point determination which showed no depression, confirmed the identity.

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DEFINITION OF STEADY MOTION

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1. The state of 'steady motion' of a dynamical system implies that among other features, it preserves, as a whole, the same *quantity* and *quality* of motion for all time. The system must therefore be conservative, as the presence of any dissipative force would continually tend to bring the system to rest.

2. A conservative system is characterized by

$$T + V = \text{constant},$$

where T denotes the kinetic energy and V the potential. This condition, it may be observed, determines the *quality*, but not the *quantity* of the motion. In fact during the whole course we have a constant interchange between the kinetic and the potential energies, decreasing or increasing the *quantity* of motion. One naturally feels inclined to investigate the special features of those modes of motion of a conservative system in which this mutual exchange, or conversion of the two types of energies is stopped.

Definition : The type of motion in which both the kinetic energy T and the potential energy V remain *separately* constant is called steady motion.

It may be claimed in favour of this definition that it is independent of any choice of the co-ordinate system, and that it has a physical interpretation.

3. In his book on Analytical Dynamics (page 193), Whittaker observes : "A type of motion which presents many analogies with the equilibrium configuration is that known as the steady motion of systems which possess ignorable co-ordinates : this is defined to be a motion in which the non-ignorable co-ordinates of the system have constant values, while the velocities corresponding to the ignorable co-ordinates also have constant values."

Now ignorable co-ordinates are those co-ordinates which are not explicitly contained in L ($\equiv T - V$), although the corresponding velocities are so contained. Further a conservative system implies that T has no part independent of a velocity term and V has no part which involves a velocity term. The above definition of steady motion,

given by Whittaker, satisfies the condition of the types of energies remaining *separately* constant.

4. A slight analogy with the equilibrium position in statics may help to clear up certain points. Equilibrium configurations of a statical system are determined by writing down the condition that the potential energy is stationary. Similarly, steady motions of a dynamical system are determined by writing down the condition that the kinetic potential L is stationary. Thus we have :—

$$\delta\ (T-V) = 0.$$

But since $T + V =$ constant, $\delta\ (T + V) = 0$.

$\therefore \delta T = 0$, and $\delta V = 0$.

i.e. both T and V are separately constant.

5. *Equations of steady motion.* The condition of stationary potential energy in statics means exactly the principle of virtual work which states that the first order change in V during any disturbance, *consistent with the geometrical constraints,* is zero. In like manner, the condition of stationary kinetic potential L means that the first order change in L during any disturbance, *consistent with the dynamical constraints,* is zero. Now the dynamical constraints are the fact that the motion is conservative, that is T + V remains constant.

Now, the usual way of obtaining the equations of steady motion is to start with Lagrange equations :

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_r}\right)-\frac{\partial L}{\partial q_r}=0, \qquad r=1,\ 2,\ 3,\ \ldots\ldots,\ n.$$

Denoting non-ignorable q's by x and ignorable q's by y, the above equations assume the form :

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right)=\frac{\partial L}{\partial x} \quad \text{and} \quad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{y}}\right)=0$$

According to Whittaker's definition all $(\dot{x})$ are constant and all $(\dot{y})$ are constant. Hence

$$0=\frac{\partial L}{\partial x}$$

Thus steady motions are specified by

$$\frac{\partial L}{\partial x}=0$$

where (x) are non-ignorable co-ordinates.

Example : In the case of the usual top-motion

$$2\,T = A(\dot{\theta}^2+\dot{\phi}^2\sin^2\theta) + C\,(\dot{\psi}+\dot{\phi}\cos\theta)^2.$$

θ is the only co-ordinate which is non-ignorable. ϕ and ψ are ignorable. Hence writing for the constants

$$\theta = \alpha,\ \dot{\phi} = \lambda,\ \dot{\psi} = \mu$$

we have

$$L \equiv T - V = \tfrac{1}{2}\left[A\lambda^2 \sin^2\alpha + C(\mu + \lambda\cos\alpha)^2\right] - Mgh\cos\alpha$$

$$\frac{\partial L}{\partial \alpha} = 0$$

gives

$$A\sin\alpha\cos\alpha.\,\lambda^2 - Cn\lambda\sin\alpha + Mgh\sin\alpha = 0,$$

$$\therefore\ \alpha = 0\text{, or } A\operatorname{Cos}\alpha.\,\lambda^2 - Cn\lambda + Mgh = 0,$$

which is, as we know, the condition of steady (precessional) motion of the top.

Let us apply the present definition to obtain these equations of steady motion :—

The kinetic potential L is stationary,—Hence $\delta L = 0$.

Now L involves x-type co-ordinates, and all the velocities $\dot{x}$ and $\dot{y}$; so that

$$L = L\ (\dot{x}, x, \dot{y}),$$

As the system is conservative t will not be explicitly contained in L, there will be no term in T which is independent of any velocity, and there will be no term in V involving any velocity.

Now

$$\delta L\,(x, \dot{x}, \dot{y}) = 0$$

should lead to

$$\frac{\partial L}{\partial x} = 0,\quad \frac{\partial L}{\partial \dot{x}} = 0,\quad \frac{\partial L}{\partial \dot{y}} = 0$$

It will be seen, however, presently that the equations of the last two types are ruled out by the *dynamical constraint, viz.*, the constancy of $T + V$. $\dot{x}$ and $\dot{y}$ are contained only in T and not in V, and therefore any variations of a velocity term will change the value of T, but cannot introduce a compensatory change in V. With regard to the co-ordinate x, however, it occurs in both T and V and it is possible to change both so as yet to have $\delta\ (T + V) = 0$.

Thus the equations of steady motion, as arising out of the condition of stationary kinetic potential L, subject to the preservation of the total energy, are as before

$$\frac{\partial L}{\partial x}\,0\text{, (every } x)$$

6. The only objection that may be urged against our definition is that it still allows conversion of one type of kinetic energy into

another type of kinetic energy. Consider the case of Euler's equations of motion of a rigid body with one point fixed, there being no external forces :

$$A\,\dot{\omega}_1-(B-C)\,\omega_2\omega_3=0$$
$$B\,\dot{\omega}_2-(C-A)\,\omega_3\omega_1=0$$
$$C\,\dot{\omega}_3-(A-B)\,\omega_1\omega_2=0$$

Here, $V=0$, and $T=\frac{1}{2}(A\,\dot{\omega}_1^2+B\,\dot{\omega}_2^2+C\,\dot{\omega}_3^2)=\text{Const.}$

According to our definition this *is* a case of steady motion; according to Whittaker's definition it is not. What happens is that ω_1, ω_2, ω_3 do alter during the motion, but the total T remains constant.

It may be observed, however, that even this motion, the complete solution of which is given by means of elliptic integrals, is *periodic*, and a whole cycle of configurations is gone through repeatedly. There is thus no reason why this type also should not be called steady motion.

The case of a simple pendulum (friction excluded) is also a case of repetition of a cycle of configurations, but in this case the two types of energies do not remain separately constant. Hence this would not be regarded as a case of steady motion.

7. The connection between the definition here proposed, and Whittaker's definition has a parallel in the development of the Quantum Theory. Generalizing Bohr's quantum condition for the case of more degrees of freedom we put down,—

$$\oint \Sigma p\delta q = nh.$$

Wilson and Sommerfield then proceeded to impose this condition on *each* individual degree of freedom of the system and we have

$$\oint p_k\delta q_k = n_k h, \text{ (every } k).$$

Now Whittaker's definition of steady motion is more or less of the same nature as the Wilson-Sommerfield restriction. All the same the rational generalization is embodied in the statement

$$\oint \Sigma p\delta q = nh,$$

which corresponds to our definition.

A NOTE ON REAL NUMBER, INFINITY AND CONTINUITY

BY

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REAL NUMBER

1. Every respectable text book on Analysis will need to begin with a discussion about rational numbers and then proceed to notice their insufficiency for various geometrical and other mathematical requirements. The search for a number whose square should be 2 by the usual arithmetical process is a failure as the process can never end ; but the numbers 1, 1·4, 1·41, 1·416, 1·4167.... obtained during the process in endless succession are such that the difference of 2 from $(1)^2$, $(1{\cdot}4)^2$, $(1{\cdot}41)^2$, $(1{\cdot}416)^2$....could be made less than any rational positive ε if we went sufficiently far along the list. These qualities were held to be sufficient justification for the *axiomatic existence* of $\sqrt{2}$ and the endless list was supposed to be a rational approach to $\sqrt{2}$ by way of approximation.

[1·1] This stand-point was far from being precise and the discussion was continued by DEDEKIND who perhaps noticed a similar behaviour for the succession 2, 1·5, 1·42, 1·417....obtained by increasing the last digit of every member by one and formulated the properties that (1) every member of the first list is less than every member of the second, (2) it is possible to choose a member in the first and a member in the second such that their difference is less than any positive rational ε, and (3) there can be no greatest in the first and no least in the second. The last step was to associate *all* rational numbers in such a classification and define a real number as a section of *all* rational numbers, possessing the following qualities :—

(1) That every rational number belongs to one and only one of the two classes.

(2) Every member of the L-class is less than every member of the R-class.

(3) Members of both classes exist.

[1·2] The discussion was also taken up by CANTOR who first noticed that in the original list, the difference of any two members coming after a certain stage could be made less than any rational

positive number ε and so was led to imagine a real number as the characteristic of such a Cantor sequence $\{a_n\}$. The objections to such a scheme are (1) that the desired characteristic or quality of such a Cantor sequence, has to be shown to be unique ; but this difficulty can be got over by defining the real number as the class of all equivalent Cantor sequences [two Cantor sequences $\{a_n\}$, $\{b_n\}$ are said to be equivalent if $|a_n - b_n| <$ any positive ε (rational) for all $n > N$], (2) the condition $|a_n - a_m| < \varepsilon$ for all n, $m > N$ constituting a Cantor sequence is far too important and difficult to be used in the construction of a real number. Otherwise it should be noted that the primary operations of mathematics can be very easily defined as $\{a_n + b_n\} = \{a_n\} + \{b_n\}$ *etc*....

[1·3] Going back to the Dedekind section, one can note only two possibilities, (1) either the L-class has the greatest and the R-class no least, or the R-class has the least and the L-class has no greatest, and (2) neither the L-class has the greatest nor the R-class the least. In the first alternative the real number is said to be *rational real*, in the second, *irrational real.*

[1·4] In proceeding to define, for Real Numbers, the idea of order (equal to, greater and less) and the operations of addition, multiplication, subtraction and division, considerable difficulty is experienced ; *e.g.*

(1) The rational real number m can be either the section with the rational m in the L-class or in the R-class. The two sections not being identical, the definition of order cannot be constructed in a simple way.

(2) The two irrational real numbers $2-\sqrt{2}$ and $\sqrt{2}$ have to have their sum the rational real number 2 ; but the rational number 2 escapes classification in the sum-section which cannot therefore be called a Dedekind section, unless the rational number 2, by a supplementary definition, be joined on to one of the sum-classes. A similar remark is true for the product-section, say, of the irrational real numbers $\sqrt{2}$ and $1/\sqrt{2}$.

(3) The definition for the product of two real numbers has to proceed by two stages. Firstly, for the case of two positive real numbers ; and then for the case when one of them is negative. Even then, the product-classes are created out of the positive rational numbers of the respective classes and all negative rational numbers are joined on to the product L-class.

[1·5] These and other similar difficulties can only be got over by hedging and supplementing the various definitions constantly. Any improvement on this should proceed towards simplifying the

construction of a Real number and also the mechanism required for defining the primary operations afterwards. The following is substantially the suggestion advanced by Bertrand Russel and effects a certain amount of simplification in the direction desired.

[1·6] Instead of the two classes or segments of a Dedekind section, only one of them, preferably the *right segment*, without its least, is defined to be a real number. This *Dedekind segment* of rational numbers is conditioned by—

(1) If x is a member, then every y, larger than x, is also a member,

(2) there are some rational numbers belonging to it and some rational numbers not belonging to it,

(3) there is no least.

A Real number a is said to be rational real if there exists a rational number m such that the segment of all xs $> m$ is identical with the a-segment, then the rational number m is said to correspond to the *rational real number a*, otherwise the real number is said to be *irrational real.*

a is said to be $= b$ when the a- and b-segments are identical.

a is said to be $<b$ when the a-segment contains at least one rational number not belonging to the b-segment.

a is said to be $> b$ when the b-segment contains at least one rational number not belonging to the a-segment.

The sum segment of the a- and b-segments is defined to be $a + b$, $-a$ is defined to be the segment formed by changing the sign of all the rational numbers not belonging to the a-segment and dropping its least if it happens to have one.

The product of a and b when both are positive is defined to be the product segment ; a modification will be necessary if one of these is negative.

$1/a$ (for a positive) is the segment formed of the reciprocals of all the positive rationals not belonging to the a-segment and then dropping the least if necessary. In this respect, as well as for the Dedekind theory, *it is preferable to take zero as an irrational real number,* as zero will not then take any part in the sections or segments and the reciprocal of zero will not trouble us.

[1·7] A similar Dedekind segment of Real numbers may be constructed, but, as it can easily be proved to correspond always to a real number, there is no prospect of obtaining new numbers (say, super real numbers).

[1·8] Starting from the idea of signless integers (or more precisely the inductive numbers) and denoting their type, say as A, integers, qualified by sign such as $+4, -3$, etc., are defined as certain relational numbers and their *type* is naturally different, say B. Fractions are still another *type* of relational numbers, say C and real numbers, a fourth *type* of relational numbers, say D. If there could be an advantage in formulating segments of real numbers, the resulting new numbers will have to be described as being of an E *type*. There is a correspondence between 2 and $+2$, between $\frac{1}{4}$ and $\frac{1}{4}$-segment but none of them is identical with its correspondent.

[1·9] The rational numbers can be put in correspondence with the rational points of a straight line. Such a correspondence for real numbers can only be effected *by axiomatically assuming the existence on a straight line of irrational points* as the lower boundaries of irrational segments. Then only the correspondence between real numbers and points of a straight line will be complete. If the straight line was found to contain in a Euclidean sense points to correspond to $\sqrt{2}$ and $\sqrt{5}$, etc., it should not follow that it must naturally contain points corresponding to all irrational numbers. The complete *irrational content* of a straight line has to be constructed by definitions parallel to those constructed for the real number theory. This full content of the straight line is called the *Geometrical continuum.*

[1·9] *Arithmetical continuum* is merely another term for the Real number group; it corresponds to the Geometrical continuum. But, it is unfortunate that it occasionally misleads one to suspect some type of *continuity* in the real numbers, as the concept of *continuity* in mathematics is always a relative one,—relative to a particular background or medium, or relative to a point of view. The quest for absolute continuity is logically defective.

LIMIT $n \to \infty$ OF A SEQUENCE

[2] A group of numbers, in an order placing all of them in correspondence with the natural numbers in their order of magnitude, is defined as a sequence $\{a_n\}$. If, for this sequence, we can find a real number a such that $|a_n - a| < \varepsilon$ (any positive number) for all $n > N_\varepsilon$ the sequence is said to tend to the limit a and we express it symbolically as $\underset{n \to \infty}{\mathrm{Lt}}\, a_n = a$. It should be noted that a symbolical statement such as $\underset{n=10}{\mathrm{Lt}}\, a_n$ can also be given the meaning $a_{10} = a_{10}$. The sequence was examined for the 10th rank. The expression "for all $n > N_\varepsilon$ describes a *Joint point of view, i. e.,* the point of view of all members of the sequence whose ranks are larger than

some N [perhaps it is preferable to be more careful and say for all ranks less than $\aleph$ (aleph) and greater than some N]. Hence the symbolic suffix $n \to \infty$ to the statement $\underset{n\to\infty}{\mathrm{Lt}}\ a_n = a$ briefly describes one point of view in respect of which the sequence is being examined. It may be read out as n tending to infinity but *the infinity used here is purely a description of our point of view.* Next when a sequence $\{b_n\}$ is such that $b_n > P$ (any real number) for all $n > N_\varepsilon$, we express this new behaviour symbolically as $b_n \to \infty$ as $n \to \infty$. $b_n \to \infty$ describes this new behaviour when the sequence $\{b_n\}$ is examined from the point of view described by $n \to \infty$. If it is also the practice to say that b_n tends to infinity, *this infinity must be of a different type from the infinity of $n \to \infty$, because $b_n \to \infty$ describes a behaviour and $n \to \infty$, the point of view.* A behaviour is a different type from the point of view. These shades of differences in the meanings of ∞ are also different from the meanings of the many transfinite numbers.

CONTINUITY

3. Functions may be of various types : functions defined for an integral variable, a rational variable or a variable described by an aggregate of numbers, say G. The study of a function in Analysis begins with noting its value at a and then finding if it is also defined for all the xs of G in a neighbourhood of a. If, for any positive ε all these values differ from $f(a)$ by less than ε, we say that the function is continuous at $x = a$ in the G variable, or symbolically the condition is $| f(x) - f(a) | < \varepsilon$ for $| x - a | < \eta$, the xs being also members of G, or for all xs of G in the interval $a - \eta$ to $a + \eta$ or still more briefly $\underset{xG\to a}{\mathrm{Lt}} f(x) = f(a)$. *The suffix $xG \to a$ describes, as before one point of view and the continuity that we have defined is then a quality of the function at $x = a$ from the point of view of G-variable.* In view of this, a function can be continuous at a place in one aggregate and discontinuous in another aggregate, *e.g.*

If $f(x) \equiv 1$ for $x = n/(n+1)$ all integral n.
$f(x) \equiv 2$ for $x = (n+1)/n$ all integral n.
$f(1) = 1$.

$f(x)$ is continuous at $x = 1$ in the variable G_1 $\{n/(n+1)$ and $1\}$ and discontinuous in the variable G_2 $\{(n+1)/n$ and $1\}$.

(2) $\phi(x) \equiv 1$ x rational.
$\phi(x) \equiv 2$ x irrational.

$\phi(x)$ is continuous at any point in the rational variable G_1 and also in the irrational variable G_2 but is discontinuous in the real variable *i.e.*, in $G_1 + G_2$.

[3·1] The usual G in Analysis is the real variable which is a *perfect* set : the idea of continuity is then constructed in relation to the arithmetical continuum. The real variable is now our medium of operation and forms the background against which every function is noticed and studied.

[3·2] Thus the mathematical notion of continuity is always relative and such as it is, it has fully served most of the purposes and needs of mathematics. The idea of anything like an absolute continuity is not necessary. As a philosophical speculation it may continue to engage the attention of many people but the structural development of mathematics can proceed without a definite conclusion being reached on this—*the absolute continuity problem.*

ON THE FOCI OF CONICOIDS

BY

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A method for determining the foci of conicoids is described in §130 of Bell's Solid Geometry. This note contains an alternative method for doing the same. We propose to illustrate it by applying to the conicoid

$$f(x, y, z) \equiv ax^2+by^2+cz^2 = 1. \qquad (1)$$

Let (α, β, γ) be a focus. Transfer the origin to it, so that equation (1) transforms into

$$f(x, y, z) + 2a\alpha x + 2b\beta y + 2c\gamma z + f(\alpha, \beta, \gamma) - 1 = 0. \qquad (2)$$

Now (2) must be of the form

$$x^2+y^2+z^2-(lx+my+nz+p)(l'x+m'y+n'z+p') = 0.$$

Hence for a suitable value of λ, we should be able to express

$$f(x, y, z) - \lambda(x^2+y^2+z^2)+2a\alpha x+2b\beta y+2c\gamma z+f(\alpha, \beta, \gamma)-1$$

as a product of two linear factors.

Hence for the same value of λ, each of the expressions :

$$(a-\lambda)x^2+(b-\lambda)y^2+(c-\lambda)z^2,$$
$$(b-\lambda)y^2+(c-\lambda)z^2+2b\beta y+2c\gamma z+f(\alpha, \beta, \gamma)-1,$$
$$(c-\lambda)z^2+(a-\lambda)x^2+2c\gamma z+2a\alpha x+f(\alpha, \beta, \gamma)-1,$$
$$\text{and } (a-\lambda)x^2+(b-\lambda)y^2+2a\alpha x+2b\beta y+f(\alpha, \beta, \gamma)-1$$

could be put in the form of a product of two linear factors. Hence we have

$$(a-\lambda)(b-\lambda)(c-\lambda) = 0; \qquad (3)$$
$$(b-\lambda)(c-\lambda)(a\alpha^2+b\beta^2+c\gamma^2-1)-(b-\lambda)c^2\gamma^2-(c-\lambda)b^2\beta^2 = 0; \qquad (4)$$
$$(c-\lambda)(a-\lambda)(a\alpha^2+b\beta^2+c\gamma^2-1)-(c-\lambda)a^2\alpha^2-(a-\lambda)c^2\gamma^2 = 0; \qquad (5)$$
$$(a-\lambda)(b-\lambda)(a\alpha^2+b\beta^2+c\gamma^2-1)-(b-\lambda)a^2\alpha^2-(a-\lambda)b^2\beta^2 = 0. \qquad (6)$$

From (3), (4), (5), (6), we get the three alternative sets :

$$\lambda = a, \;\; \alpha = 0, \;\; \frac{\beta^2}{a^{-1}-b^{-1}}+\frac{\gamma^2}{a^{-1}-c^{-1}}+1 = 0;$$

$$\lambda = b, \;\; \beta = 0, \;\; \frac{\gamma^2}{b^{-1}-c^{-1}}+\frac{\alpha^2}{b^{-1}-a^{-1}}+1 = 0;$$

$$\text{and } \lambda = c, \;\; \gamma = 0, \;\; \frac{\alpha^2}{c^{-1}-a^{-1}}+\frac{\beta^2}{c^{-1}-b^{-1}}+1 = 0.$$

Hence the focus (α, β, γ) lies on the one or the other of the conics :

$$x=0, \quad \frac{y^2}{a^{-1}-b^{-1}}+\frac{z^2}{a^{-1}-c^{-1}}+1=0;$$

$$y=0, \quad \frac{z^2}{b^{-1}-c^{-1}}+\frac{x^2}{b^{-1}-a^{-1}}+1=0;$$

and $$z=0, \quad \frac{x^2}{c^{-1}-a^{-1}}+\frac{y^2}{c^{-1}-b^{-1}}+1=0.$$

A similar method applies to paraboloids.

THE PLANETARY CHART AND ASTRONOMICAL PHENOMENA FOR THE YEAR 1935.

BY

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The planetary chart shown in Fig. 1 is similar to the one published before,* for the year 1934. The ordinate represents the right ascension of various celestial objects (the sun, moon and planets) and the abscissa, the time of the year. A detailed explanation of the chart regarding the interpretation of various astronomical phenomena will be found in the reference quoted above. Some of the important phenomena connected with the five principal planets, for the year 1935, are described below. It would be easy to verify them with the help of the present chart.

Mercury: This innermost of the planets is located with a little difficulty by the inexperienced eye, on account of its close proximity to the sun. It should be looked for either in the morning or evening twilight according to its position. During the earlier part of February, latter part of May and in the middle of September, it will be seen low down on the western horizon after sunset. As a morning star it makes its appearance in the months of March, July and November. The most convenient times for looking out for this planet would be about 15th March (morning) and about 23rd September (evening). On these days it is furthest from the sun, rising one and a half hour before, and setting one and a half hour after the sun, respectively.

Venus: For the major part of the year, this planet, easily the most brilliant of all, will be seen in the evening sky. It reaches its greatest apparent distance from the sun on 30th June, when it will set nearly three hours after the sun (for places near the equator), and will be visible high up in the western sky. The planet will be seen at its brightest on 3rd August, when its distance from the earth, and its reflection of sunlight, place it in a favourable position. After 10th August it follows a retrograde course and passes through an inferior conjunction with the sun on 8th September. Afterwards, it emerges on the other side of the sun and will be seen as a morning star for the rest of the year.

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*Vaidya, *Nature,* Vol. 133, p. 33, 1934,

Mars: In the beginning of the year, this planet, known for its ruddy appearance, will rise at about midnight. On 27th February, it commences the retrograde motion and will be in opposition to the sun on 6th April. At this time of the year it rises at sunset and, being in opposition, is quite bright. It will be easily located in the constellation of Virgo, near the bright star Spica, or Chitra of the Hindu mythology. At the end of the year it will be much nearer the sun, and will be seen after sunset in the western sky for about one and a half hour.

Jupiter: This planet, well known for its brilliancy, will rise about four hours before the sun, in the earlier part of the year. It passes through the opposition on 10th May. After the beginning of June, Mars will be seen approaching Jupiter day by day till 27th August, when the two will be in conjunction. Lying very close to each other, this pair would afford a splendid sight in the early part of night, above the western horizon in the constellation of Libra. The conspicuous star Antares (Anuradha) in Scorpio would be about 15° above these two planets, at this time of the year. Another interesting spectacle would be witnessed on 4th September when the moon, five days old, will be in conjunction with the two planets.

Saturn: Saturn will be seen in the earlier part of January on the western horizon, when it sets about three and half hours after the sun. No other bright star will be found near, and the planet should be recognised without much difficulty. From the middle of March and onwards it will be visible in the morning and rise earlier and earlier on successive days. It will be in opposition to the sun on 31st August, when it will naturally rise at sunset. The most convenient times for locating this planet in the latter part of the year, would be, when the moon is near enough. This happens on 15th August (next day after full moon), 12th September (full moon), 9th October (moon 11 days old), 5th November (moon 9 days old), and 3rd December (moon 7 days old).

The planets Uranus and Neptune are of little importance to the casual observer, for they are not bright enough to be seen by the unaided eye. The chart, however, shows their positions during the course of the year.

Eclipses: The year 1935 is notable for its number of eclipses, seven in all. Of these, there are five solar and two lunar. The former of these occur on 5th January, 3rd February, 30th June, 30th July and 25th December. The two latter take place on 19th January and 16th July. In India, however, out of these seven, only one, that of the moon on January 19th, will be visible. This is a

total lunar eclipse and would be visible throughout its course, beginning at about 7-30 in the evening and ending after 11 at night.

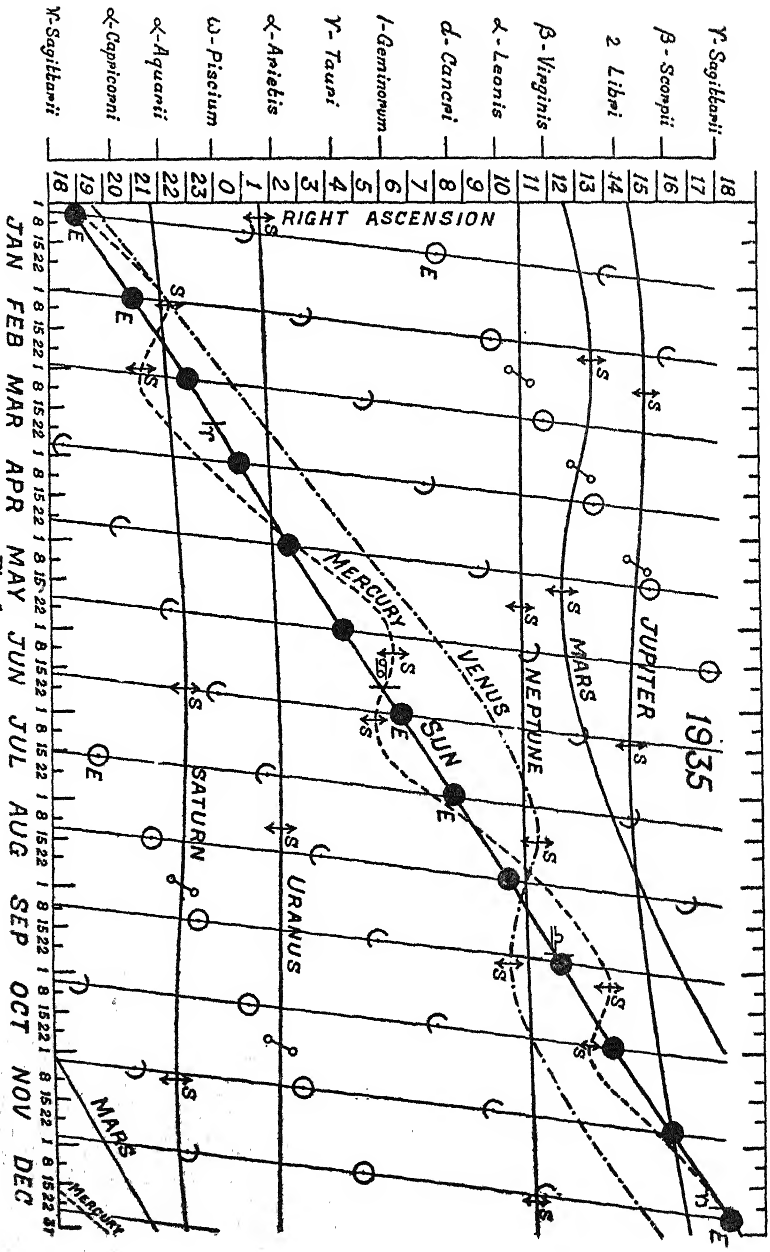

Fig. 1.

IS MATHEMATICS AN ARTS OR A SCIENCE SUBJECT?

BY

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This question has been brought up in recent years for discussion in some University meetings by those who honestly feel the awkwardness of the present position under which the Board of Studies in Mathematics belongs to the Faculties of Arts and Science.

For years past the Board of Studies in Mathematics belonged to the Faculty of Arts in this University and the Board, I presume, discharged its duties as well as now. Some of the scientists, however, felt that though Mathematics was a science, they were being deprived, unjustly they thought, of the right of a say in the appointment of examiners in Mathematics. That is what at least one pure scientist openly said, and ultimately a resolution was brought before the Senate to the effect that the Board of Studies in Mathematics should belong to both the Faculties—Arts and Science—and that each Faculty should be asked to elect four representatives on that Board, thus making up a total of eight. Some of the arguments brought forward in support of the proposition were that Mathematics was exact and was therefore more a Science than an Arts subject, that some of the science subjects and Mathematics were to a large extent interdependent, and the case was therefore clear that the Board of Studies in Mathematics should belong to the Faculty of Science. As a transitory measure or as a compromise, the mover said the Board might belong to both the Faculties with equal representation from each. The Senate passed the resolution, and the present position continues since then.

Recently some members of the Faculty of Arts felt the awkwardness of the situation. A large number of Arts subjects, especially languages and history, are independent of Mathematics and an attempt was made first to transfer the Board of Studies in Mathematics wholly to the Science Faculty. That attempt failed. An attempt was then made to remove Mathematics from the B.A. Honours Course. For the present that attempt has also not been successful.

This short history of the problem has tempted me to write the present article.

Pure Mathematics, Logic and Law are supposed to train a man's faculty in accurate reasoning to enable him to arrive at unbiassed conclusions. To what extent each subject has been successful in achieving this aim, it will be presumptuous on my part to say. I can assert, however, without fear of contradiction that pure mathematics has contributed no less than the other two subjects in training an individual in the art or science of accurate reasoning. Like Logic and Law, therefore, Mathematics is both an Arts and Science subject.

Science consists mainly of experiments and observation. From a number of experiments carefully performed, certain conclusions are drawn in a general way, and their validity tested further by additional experiments and further observation. The general conclusions once arrived at hold the field but always *pro temps* until new experiments have shown clearly that the previous hypotheses require modification. In a number of cases, the conclusions arrived at are, from the point of view of the layman, exact. The scientist is fully conscious, however, that his results are only approximately correct as his powers of observation and measurement are limited by 'personal equation' and imperfect instruments at his command. Not so in pure mathematics, where the investigator has to depend only on "paper and pencil". A proof in pure mathematics is either false or correct and conclusions are in no case obtained by experiments and observation.

In Science though the results obtained may be approximate, their utility can be hardly questioned. Many have become millionaires by their ability to adapt the results of researches in pure Science to practical concerns. Even though in many cases the investigator himself may not have become richer by his researches, there is no doubt that he has helped the middle men to reap the harvest of his labours. The researches in pure mathematics, *e.g.*, theory of numbers, theory of functions, etc., stand on a different footing altogether. I cannot do better than quote the words of Professor G. H. Hardy* :—

"But, if I am asked to explain how, and why, the solution of the problems which occupy the best energies of my life is of importance in the general life of the community, I must decline the unequal contest: I have not the effrontery to develop a thesis so palpably untrue. I must leave it to the engineers and the chemists to expound, with justly prophetic fervour, the benefits conferred on civilization by gas-engines, oil, and explosives. If I could achieve every scientific ambition of my life, the frontiers of the Empire would not be advanced, not even a blackman would be blown to

*Inaugural Lecture, 1920, Oxford.

pieces, no one's fortune would be made, and least of all my own. A pure mathematician must leave to happier colleagues the great task of alleviating the sufferings of humanity."

It will thus be seen that from the point of view of utility and from the point of view of methods of investigation pure mathematics stands on a different footing altogether from experimental sciences and has more claim to be regarded as an arts subject than a science subject. If the results of researches in pure mathematics have sometimes found applications, that is a matter of accident for which the pure mathematician must plead "not guilty".

Applied mathematics on the other hand goes hand in hand with physics and is really a branch of that subject. In physics higher researches require a wide knowledge of mathematics and hence "natural philosophy" came to be added to mathematics as a part of the subject. Mechanics, hydrostatics, hydrodynamics, electricity, magnetism, optics, thermodynamics, quantum mechanics, etc., became more and more dependent on mathematics. These subjects developed and in the interests of advancement of scientific knowledge these subjects were allowed to be added to courses of study in mathematics, and it is not uncommon nowadays to find new results in physics the background and basis of which is purely mathematical. It may well be argued that some of the latest theories advanced in physics had nothing to do with experiments and observation, as far as their origin was concerned. It is equally true, however, that they had to await confirmation from experiments and observation. Even if it were not so, it cannot lead us to dislodge pure mathematics from its position as an arts subject; it would perhaps make the claim of new physics to be regarded as an arts subject stronger.

Interdependence between mathematics and various scientific subjects cannot be urged as a plea for treating it only as a science subject. To-day many of the barriers have broken down, and if physics has always been dependent on higher mathematics, chemistry, biology and other subjects have now joined the company and no science can now boast of its proud isolation from all others. But then the same phenomena are visible on the arts side as well. For ages philosophers have been spending their precious time on mathematical conceptions of infinitesimal, infinity, etc., and Bertrand Russell and Whitehead have to-day placed before us a branch of philosophy called 'mathematical philosophy' which cannot be ignored. Thus philosophy and mathematics have become interdependent to-day. I leave it to the economists to decide whether their subject should belong to arts or to science, but I presume no eco-

nomist would come forward to say that statistics is not required in economics, at least in the higher stage, and there must be many economists who must be feeling to-day the handicap they suffer from because of their early disdain, and consequent lack of knowledge of mathematics which closes to them a fruitful field of research by statistical methods.

From all these considerations I am led to conclude that pure mathematics is an arts subject, and mathematics in all its aspects, pure and applied, may be said to be both an arts and a science subject as well.

I am strengthened in the opinion expressed above by the fact that most of the Universities in India and elsewhere have given an important place to mathematics both in their Arts and in their Science syllabuses.

COLLOIDS IN THE ATMOSPHERE*

BY

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Summary. In this article an attempt has been made to summarise the present position of the subject of "Colloids in the Atmosphere". As far as possible references to all important papers on the subject have been included. The article contains a detailed account of important properties of colloidal particles in the atmosphere with reference to some meteorological factors. Difficulties in the way of applying the ideas of coagulation of colloidal solutions to colloids in the atmosphere have also been pointed out.

GENERAL

A systematic study of disperse systems started with Graham. In a disperse system the dispersion medium may be a solid, liquid or gas; the disperse phase can exist in one or more of the conditions—solid, liquid or gaseous. Most of the investigations of colloid chemists have been directed to systems in which the dispersion medium is either liquid or solid.

Ordinarily the atmosphere at least in the troposphere can hardly be taken as only a molecular dispersion system. The atmosphere is a colloid dispersion system in which the dispersion medium is in a gaseous condition and the disperse phase in solid and liquid conditions. On the analogy of calling a system in which water is the dispersion medium a hydrosol, a system in which air acts as dispersion medium is called an aerosol. The nature and size of the particles of the disperse phase in the atmosphere vary considerably.

The disperse phase in the atmosphere plays a very important part in various meteorological phenomena. A systematic study of colloids in the atmosphere can be said to have started with John Aitken (Collected Scientific Papers of John Aitken, Cambridge University Press, 1923).

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*In preparing this article free use has been made of "Atmosphäre als Kolloid" by Schmauss and Wigand, "Clouds and Smokes" by Gibbs and of other scientific papers and books mentioned in the body of the text.

SMALL IONS

The classification of the disperse phase in the atmosphere is generally based on the size of the particles of the dispersed component.

When air is exposed to ionising agents such as radiations from radio-active substances, ultra-violet rays from the sun and cosmical penetrating radiation, the molecules of the atmosphere get ionised. These ionised molecules collect round other molecules of air, water vapour or carbon dioxide and become molecular aggregates which are usually designated as small ions. These small ions may be charged either positively or negatively.

The size of the small ions has been calculated by various investigators by their movement in an electrical field as well as from the condensation effect. In an atmosphere of normal humidity they move with a speed of 1 to 2 cms. per second in a field of one volt per centimetre and this speed generally decreases with an increase of humidity. Also the negative ions generally move faster than the positive ions. The radius of the small ion is 3 to 4 $\times$ 10^{-8} cm. according to calculations of J. J. Thomson (see Applications of Dynamics to Physics and Chemistry) and Chauveau (Le Radium, 9, 161, 1912). According to Loeb (Ann. d. Phys., 84, 689, 1927) the number of molecules in a normal small ion does not exceed 6 while according to Lenard (ibid., 41, 91, 1913) it is more than 9 of the magnitude O_2 molecules. As more and more new small ions are formed some of the old ions are removed by reunion and therefore their number cannot go on increasing indefinitely. Nolan (Proc. Roy. Irish. Acad., 41, 61, 1933) has observed that at high concentrations the rate of disappearance of small ions is proportional to the concentration; he further argues on this basis that the former is a result of coagulation while the latter of diffusion. According to Hess (Wien. Ber. [2 a] 136, 603, 1927; Phys. Zeit., 28, 882, 1927) the average life of small ions is about 30 seconds.

On an average the number of small ions of one sign comes out to be about 700 per c.c. Mathias (Gerlands Beitr. z. Geophys. 27, 360, 1930) has determined the small ion content of the atmosphere at Heligoland and found that the relative humidity shows correlation with the ratio of the number of small positive ions to the number of small negative ions. He has also found a remarkable relation between the number of small ions on the one hand and the direction of wind, transparency, sunshine etc. on the other. J. J. Nolan and P. J. Nolan (Gerlands Beitr. z. Geophys., 25, 414, 1930) have observed that the ratio of positive to negative small ions is about 1·45, there being thus an excess of positive small ions.

The vapour pressure over a convex surface (presuming that spherical drops are formed) being greater than over a plane surface (the smaller the radius of curvature the greater the vapour pressure) one may be inclined to think that condensation may not take place on these small ions, for the very fine drops may evaporate no sooner they are formed. However, as stated before, these small ions are electrically charged—every ion probably carries at least an elementary charge $e = 4{\cdot}77 \times 10^{-10}$ E.S.U.—and the presence of the electric charge diminishes the vapour pressure to an extent that is proportional to the fourth power of the radius of the drop. On the basis of this relation it is found that the vapour pressure over the charged drop when compared with that over a plane surface increases with the increase in the size of the drop till r becomes $0{\cdot}63\mu\mu$; if the drop increases further in size the vapour pressure however begins to decrease. It will thus be seen that charged droplets whose radius is greater than $0{\cdot}63\mu\mu$ can act as nuclei for condensation. As stated before, the radius of the small ions is of about this order and hence, as a result of the electric charge which they carry, the effect of curvature will not be felt and they will be able to act as condensation nuclei. Thus the electric charge plays the role of hygroscopic agent inasmuch as it can lower the vapour pressure and facilitate condensation of water vapour even when there is low degree of supersaturation. The fact that condensation takes place on such charged ions has been conclusively proved by the classical experiments of C. T. R. Wilson (Phil. Trans., 189, 265, 1897 ; 192, 403, 1899).

In view of the greater size of positive ions than that of negative ones one would expect that condensation should take place at lower values of supersaturations in the former case than in the latter. Wilson's (loc. cit.) experiments have, however, conclusively shown that condensation takes place on negative ions at supersaturation value S=4 and on positive ions at S=6.* Schmauss and Wigand (Atmosphäre als Kolloid, 1929, S. 3) think that the cause of this peculiar behaviour might lie in the different magnitudes of the electric forces which work between negative and positive ions on the one side and water molecules on the other side ; water vapour possesses polar properties on account of its constitution and condensation takes place more easily on negative than on

*$S=C_1/C_2$, where C_2 is the concentration of the water vapour in the air after adiabatic expansion to volume V_2 and temperature T_2 and C_1 is the concentration of water vapour in the air immediately before expansion when volume is V_1 and temperature is T_1 ; V_2/V_1 is the expansion ratio or expansion.

positive ions. Sir J. J. Thomson (Conduction of electricity through gases, Vol. I, 1928, p. 332 et seq.) considers that at the surface of a water drop there is a double layer of electrification, *i.e.* a layer of one sign at the surface of the drop and a layer of opposite sign in the gas, the distance between the two layers being very small. He has further shown mathematically that if a layer of this kind existed, it would produce a difference between the condensing powers of positive and negative ions. According to this the layer will make an ion of the sign which produces at the surface of the drops an electric field in the same direction as that due to the double layer, more effective as a condenser than an ion of the opposite sign. Thus if the double layer in the case of water had the negative coating inside, a negative ion would be more effective in producing condensation than a positive one. When a fresh surface of water is exposed to air the latter gets negatively electrified and equal quantity of positive electricity goes to the water surface to form the outer coating of the double layer, so that double layer has the negative side next the water, the positive side next the air.

Wilson (loc. cit.) has also found that, at values of supersaturation 8 or more, the condensation can take place in the absence of any Aitken or charged nuclei, the size of drops decreasing upto value of S=12 after which the drops again become coarser. If the size of drops decreases with an increase in the number of drops, there being available the same amount of vapour for condensation, it can be taken to mean that the number of drops produced at S=12 is a maximum, it being less for higher or lower values of S. At values of S=8 or more the molecules of water vapour themselves act as condensation nuclei. This behaviour of water vapour is similar to the behaviour of supercooled melts and supersaturated solutions (also see Freundlich, Colloid and Capillary Chemistry, Eng. Trans. 1926, p. 769); it has been shown that the velocity of formation of nuclei passes through a maximum in this way as the temperature falls and the supercooling or supersaturation increases.

Usually the atmosphere does not contain the amount of water vapour sufficient to saturate it. However under favourable conditions it gets saturated with water vapour. From the efficiency of small ions as nuclei for condensation of water vapour, which has been discussed above, it will appear that under ordinary conditions they may not serve as condensation nuclei. Kopp (Beiträge z. Physik der frein Atmosphäre, 14, 169, 1930) has adduced evidence to show that a relative humidity of even 300 to 600% is sometimes met with in clouds and under such circumstances the small ions may be able to serve as condensation nuclei. Numerous humidity mea-

surements by Conrad and Wagner (Monthly Weather Review, 11, 436, 1928) on Sonblick in the most dense clouds have shown average values of 102·5%, with an absolute maximum of 107% (also see L. H. G. Dines, Nature, 132, 938, 1933). Evidence of supersaturation sufficient for condensation to take place on small ions has also been brought forward by A. Wigand (Ann. d. Phys. 59, 721, 1919). During his flights at heights of about 9000 metres he noticed that dense clouds formed when air was breathed out and this is due to the fact that the exhaled air at the temperature of the human body is suddenly cooled to about — 40°C., thus giving rise to supersaturation sufficient for condensation on small ions; if supersaturation is, however, more than eightfold, condensation may take place on water vapour molecules themselves. Whether the drops formed as a result of supersaturation will remain in liquid condition or solidify will depend on the temperature. The exhaled air itself does not contain any condensation nuclei as has been shown by A. Wigand (Meteorol. Zeit., S. 10, 1913).

LARGE IONS

Langevin (Compt. rend. 140, 232, 1905) in the course of his study of the nuclei in the atmosphere came across charged ions which were larger and also moved much slower than the small ions; these are known as large or heavy ions and also as Langevin ions. They are formed generally as a result of adsorption of small ions and electrons by the small neutral liquid or solid particles in the atmosphere. They can also be produced as a result of photochemical action which takes place in the atmosphere due to ultra-violet light from the sun; the light as it passes through air ionises the constituent gases and at the same time produces traces of such hygroscopic compounds as NH_3, H_2O_2, NO_2, etc. These large ions are generally found in considerable amount in the atmosphere over towns or industrial centres. This is partly due to the fact that the smoke from the chimneys sometimes contains some fine particles of sublimation products as well as SO_3; the latter specially is very hygroscopic and can form nuclei for condensation even in unsaturated air, the drops being stable as a result of lowered vapour pressure. Similarly the salt particles left in the air as a result of the evaporation of sea spray also act as very good condensation nuclei due to their hygroscopic nature. Owens (Proc. Roy. Soc., 110, 738, 1926) has observed that in various sea fogs the nuclei began to gather moisture to themselves at relative humidity of about 74 per cent. Pick (Q. J. Roy. Met. Soc., 58, 165, 1932) has shown that not only do fogs occur in unsaturated air but that saturated air is not necessarily accompanied with fog. These fine liquid drops though origi-

nally uncharged can get charged as a result of adsorption of small ions or electrons at their surface. From their movement in electrical field as well as the condensation effect their radius is estimated to be of the order of 10^{-6} cm. (Lenard, Ann. d. Phys., 1, 486, 1900 ; 3, 289, 1900 ; Meteorol. Zeit., S. 150, 1912 ; Chauveau, loc. cit. and Booth, J. and Proc. R. Soc. New South Wales, 57, 173, 1923 ; Meteorol. Zeit., S. 251, 1925). Light scattering experiments give the value of r to be about $5{\cdot}5 \times 10^{-6}$ cm. (Maclaughlin, Compt. rend. 184, 1183, 1571, 1927). They move with a speed of about 0·0005 cm./sec. in a field of one volt per centimetre.

Nolan and De Sachy (Proc. R. Irish Acad., 37, 71, 1927), Pollock (Le Radium, 6, 129, 1909 ; Phil. Mag., 29, 514, 636, 1915) and Gockel (Neue Denksch. d. Schweiz. Natur f. Ges., 54, Abh. 1, 1917) have discovered in the atmosphere ions which are of an intermediate size greater than small ions and smaller than big ions. They move with a speed of about 0·01 to 0·05 cm./sec. and have radius about 4×10^{-7} cm. In their property they very much resemble large ions. Hogg (Gerlands Beiträge zur Geophysik, 41, 1, 1934) has also detected presence of intermediate ions in Australia ; they have been found to carry only an elementary charge. The ratio of the number of intermediate and large ions varied with the meteorological conditions.

The large ion content of the atmosphere varies with locality. In very recent measurements Isräil (Gerlands Beitr. z. Geophys., 23, 144, 1929 ; 26, 283, 1930) has determined the ratio of large ions to small ions and found it to be about 6-7. Thus about 15% of nuclei were found to be charged. The number of large ions was found to decrease with improved visibility and decreased humidity. He also analysed the results with reference to air masses and found that polar air shows fewer large ions than tropical air, the number being least for old polar air and low humidity and most for mixed air at surfaces of discontinuity. The dust nuclei variation was similar to the large ions. He also observed that the number of large ions (also dust nuclei) was maximum in winter and minimum in summer, the variation of small ions being in a reverse direction. The changes were found to be maximum at 4 and 14 hrs. and minimum at 8 and 13 hrs.

The investigations of Nolan, Boylan and De Sachy (Proc. R. Irish Acad., 37, 1, 1925) and of Arendt and Kallmann (Zeit. f. Phys., 35, 421, 1926) on fog particles have shown that the big ions carry only an elementary charge. Thus in the case of these big ions in consideration of their magnitude, the charge which they carry does not appreciably affect condensation. Those of the big ions which

do not contain hygroscopic substances require a supersaturation of a few per cent. in order to act as nuclei to produce visible fog particles (Gockel, loc. cit.; Booth, loc. cit.). It has been observed by Pollock (loc. cit.) that the size as well as rate of movement of the big ions changes with a change in humidity. Torrenson and Wait (Terr. Mag. and Atmos. Electricity, 39, 47, 1934) have determined the number of large ions and uncharged ions for Washington and found that the ratio of the latter to the former comes to about 6; most of the large ions were found to carry only an elementary charge but some of them had also double charge.

The big ions move very slowly under gravity. Ions of radius 10^{-6} to 10^{-7} cm. fall according to Stokes-Kirchoff formula only at a rate of 2×10^{-5} cm./sec. or less than 1 mm./hr. The small ions which are of a still smaller magnitude will move much slower than the big ions. Both these air ions, however, move at an appreciable rate in the electrostatic field of the earth. The big ions in a normal vertically directed field of 1 volt/cm. travel at a rate of 5×10^{-4} cm./sec.; but during a thunderstorm when a vertical field strength of 1 kilovolt/ cm. is not at all unlikely, they move at a rate of 0·5 cm./sec., or during a lightning discharge when the field may be 100 times greater they move even at a rate of 5 cms./sec. The small ions move in ordinary earth's field at a rate of 1 cm./sec., but in a thunderstorm field or when a lightning discharge takes place they can move as fast as 10 metres/sec. and 100 metres/sec. respectively.

DUST

The atmosphere also contains dust particles of varying sizes. In this we can include cosmic dust, *i.e.* the particles which come from meteors. A regular and a large supply of dust particles in the atmosphere comes, however, from the surface of the earth as a result of wind which loosens the particles from the liquid or solid crust and carries them into higher levels of the atmosphere. These particles if uncharged will gradually settle down according to Stoke's law. During the day when the earth's surface gets heated convection currents are set up and they help to keep the dust particles in suspension. Also during volcanic eruptions a considerable amount of impurity is added to the atmosphere. These products of volcanic eruption are sometimes carried to very great heights and travel round the earth several times and also produce brilliant colours at sunrise and sunset. One such very famous eruption of Krakatoa occurred in the year 1883.

Some of these dust particles in the atmosphere also carry electric charge and this charge is considerably greater than the charge

carried by the small and big ions. The charge might have been acquired as a result of adsorption of gaseous ions at the surface of the particles or due to friction. Rudge (Phil. Mag., 23, 852, 1912; 25, 481, 1913) has shown that the nature of the charge on dust particles when they are blown about in the air depends on the chemical composition of the dust. Generally speaking non-metallic dust and dust of acid forming oxides becomes positively charged, metallic dust and dust of basic-forming oxides becomes negatively charged and in the case of salts the charge depends upon relative strength of the acid and basic ions. The electric charge carried by the dust particles produces considerable changes in the atmospheric potential gradient. The mineral dust particles are considerably larger than the big ions.

The atmosphere also contains fine particles of carbon as a result of smoke from the fires. The number of carbon particles is generally largest in the air of industrial towns and of forests where fires are very active.

Regarding the condensation effect it may be stated that only those dust particles which are chemically or physically hygroscopic act as effective condensation nuclei (Wigand, Meteorol. Zeit., S. 10, 1913; also Ann. d. Phys., 59, 693, 1919). Measurements of H. Koppe carried out in Öilberg in Jerusalem in 1916-1917 have shown that the east wind which appears there as dry sirocco brings with it very large amount of dust from the desert and reduces visibility considerably; in this air mass the condensation nuclei per c.c. were found to be very few. On the other hand, in the west wind which blows from sea the number of nuclei was about 2000 per c.c. C. Braak (Verb. Konk. Magn. en Met. Obs. Batavia, No. 10, S. 14, 1922) has also found that the usual dust clouds are poor in nuclei. Wigand (loc. cit.) and Boylan (Proc. Roy. Irish Acad., 37, 58, 1926) have observed that non-hygroscopic dust particles do not act as nuclei even in supersaturated atmosphere.

HYDROMETEORS

Besides the small and big ions and dust particles mentioned before, the atmosphere also contains solid or liquid particles produced as a result of the condensation of water vapour contained in it. These solid or liquid particles separate out as a result of supersaturation and are commonly known as hydrometeors in order to distinguish them from the real precipitation. The action of gravity on the hydrometeors is not appreciable. Their horizontal movement depends upon the wind velocity at their own level. The magnitude of the hydrometeors varies considerably. The diameter of the haze

particles which are visible has been estimated to be below $2{\cdot}5 \times 10^{-5}$ cm. by A. Wegener (Thermodynamik der Atmosphäre, Leipzig, 1911, S. 251). The haze particles which are larger are termed fog particles, the lower drop magnitude of which lies near 4×10^{-4} cm. and the upper limit near 3×10^{-3} cm. In country fogs in England the number of fog droplets is sometimes as great as 1500 per c.c. The drops in the clouds are generally bigger than fog particles and the radius may be even of the order of 1×10^{-2} cm. The radius of the rain drops may range from 1×10^{-3} to nearly 0·2 cm. These liquid or solid particles may be charged if condensation has taken place on ions or may get charged by adsorption of ions on the surface. If the temperature is sufficiently low the water vapour condenses to fine ice needles. The words fog and cloud are generally used loosely. As mentioned by Humphreys (Physics of the Air, 1929 Edition, p. 273) "fog is a cloud on the earth ; cloud is a fog in the sky".

NUMBER OF CONDENSATION NUCLEI

Numerous investigations have been carried out for determining the number of nuclei on which condensation can take place on small adiabatic expansions of air in different localities and under different weather situations. The number of nuclei per c.c. under different conditions comes to be

1000 — 10,000	Cyclonic (barometric depression) weather.
10,000 — 100,000	Anticyclonic (barometric high) weather.
> 100,000	Big town and industrial centres.
100	Pure land air and in hills.

Wigand (Ann. d. Phys., 59, 693, 1919) has determined the number of nuclei at different heights in an anticyclonic weather situation and obtained the following results:—

Height in Metres.	Number per c.c.	Cloud stage.
100	44,000	
500	13,000	Stratus and Cumulus.
1,000	5,000	
2,000	550	
3,000	200	Alto-Stratus and Alto-Cumulus.
5,000	50	
8,500	5	Cirrus.

Rain, high wind and especially Föhn wind caused marked decreases in the number of nuclei (Hess, Gerlands Beitr. z. Geophys. 28, 129, 1930). Intensity of sunshine or transparency of the atmosphere was found to be ineffective in controlling the number of con-

densation nuclei. Nuclei were fewest with medium humidity and cloudiness was found to have no influence except when it was raining. Highest numbers coincided with high and steady barometer and lowest with falling one. There was also some indication of low numbers preceding by some 12 hrs. change in the weather, pointing to a possibility of local forecasting. Wright (Met. Office, London, Geophy. Mem. No. 57, 1932) has also observed that number of condensation nuclei at Kew is affected by wind and humidity but not by cloud.

On plotting log K (number of nuclei per c.c.) against height, Wigand found that the curve was not uniform but consisted of three straight line pieces with kinks at 1750 and 3000 metres height. According to him this indicates a stagewise layering corresponding to the most frequent heights at which different types of clouds form, *e.g.* in this case stratus and cumulus and alto-stratus and alto-cumulus respectively. Wigand has expressed the variation of nuclei (K) with height (h) in each stage by the formula :

$$h_2 - h_1 = x \; (\log K_1 - \log K_2)$$

In every stage the factor 'x' has a different value. This expression fitted well with his results. Hess (loc. cit.), however, found that Wigand's formulæ did not hold for his results.

CHEMICAL COMPOSITION OF THE CONDENSATION NUCLEI AND SIZE OF WATER DROPS IN CLOUD AND FOG

It has been stated before that considerable supersaturation is necessary for the small ions in the atmosphere to act as nuclei. In view of this it may be taken that in the lower levels of the atmosphere (below the cirrus level) they may not usually act as condensation nuclei. The big ions, however, require proportionately much less degree of supersaturation and may act as condensation nuclei even in lower levels. H. Bongards (Monthly Weather Review, 11, 437, 1928) has tried to show a statistical relation between density of big ions and fog formation and come to the conclusion that presence or absence of big ions as nuclei was the cause of greater or lesser fog frequency at Lindenberg.

Aitken (loc. cit.) on the basis of a series of interesting experiments came to the conclusion that it is mostly the hygroscopic nuclei (See section on "Large Ions") which effect condensation under ordinary circumstances because in such cases condensation can take place even in unsaturated air. In industrial centres one finds presence of SO_3, tar and other insoluble matters. Köhler (Series of papers in Geofysiske Publikationer of Oslo and in Met. Zeit.) has made observations

at Partetjakko in Sweden and at Haldde Observatory in North Norway and come to the same conclusion as Aitken about the effectiveness of hygroscopic nuclei in condensation. Of about 4000 humidity measurements taken in Sweden and Norway he found only four or five showing supersaturation. His observations apparently do not support Kopp's results about supersaturation.

Köhler's measurements (this is taken from Willett's article in Monthly Weather Review, 56, 435, 1928) were taken for the greater part at temperatures below 0°C., the lowest being −28°C. He made the following principal observations, chiefly at Haldde (900 metre elevation) but to a lesser extent also at Partetjakko (1850 metres elevation):—

(1) Relative humidity with respect to water rarely exceeded 100%, never by more than one half per cent; relative humidity with respect to ice, however, was frequently greater than 100%.

(2) Fog-frost deposits at whatever temperature laid down showed clearly under the microscope that they were formed by the deposition and freezing of supercooled droplets, not by sublimation in crystalline form. Furthermore the microscopic examination showed that precipitation in the solid form apart from hail, had three forms : (*a*) fine snow crystals the product of sublimation, (*b*) snow crystals more or less covered and melted by the deposition and congealing of supercooled droplets, and (*c*) ice clumps produced by the meeting and congealing of two or more supercooled droplets.

(3) On the average 13 out of 20 fog droplets belonged to a series whose sizes increase as 1, 2, 4, 8, 16, 32; the most frequent size of drops of this series being 0·07 mm., he called the series the "7 series". He also found traces of an "8 series". From certain coronal characteristics in such clouds, which he detected also in coronas produced in alto-stratus and cirrus clouds, he concluded that the same series exist among supercooled droplets in the highest cloud levels.

(4) Numerous tests applied to fog-frost deposits showed an almost constant chlorine amount, 3·59 mgm. per litre, just 1/10,000 the concentration in sea water. Quantitative tests for magnesium showed the same ratio to chlorine amount as exists in sea water, and the presence of calcium was proved qualitatively. Köhler tried, by choosing the fogs whose deposits he had tested according to the size of the prevailing droplets, to test the sea salt content of each droplet series, and he came to the conclusion that only the "7 series" contributed actively to these deposits; for the "8 series" he considers that the nuclei are derived from the plant world or from the nitrogen compounds which are present in the atmosphere. He found that pure

snow flakes had no chlorine content, those with frozen droplets attached showed chlorine amounts increasing with the number of droplets, while the ice clumps showed the same chlorine amounts as the fog-frost deposits.

Köhler's results seem to be supported by observations of Kinch (at Cirencester, England, 1885-86) in which he found that winter rain water contained 3·58 mgm. of chlorine per litre, approximately Köhler's value; A. Defant (Meteorol. Zeit., S. 321, 1905 ; also see Schmidt, ibid., S. 496, 1908 ; F. Albrecht, Sonnblick—vereins—bericht, S. 11, 1924) found for Vienna, an inland station, a chlorine quantity only two-thirds of the value of Köhler. The results of Defant (loc. cit.) and Niederdorfer (Met. Zeit., 49, 1, 1932) also show existence of drop series.

According to Köhler's results one has to assume that salt particles or droplets of only one particular size are driven from the sea. One will expect that the size of droplets driven from the sea surface will depend on the strength of the wind blowing over sea and as such droplets of different sizes may be driven from the sea. Köhler's work also shows that there is a greater attraction between drops of the same magnitude than between those of different magnitudes, a fact which has not been observed in other colloidal phenomena. On the contrary it is a common experience to find that there is always a tendency for smaller particles to unite with the relatively larger particles or as is popularly called the larger particles grow at the expense of smaller ones. Also it is not clear why the "7 series" drops should invariably contain ingredients of sea salt, while the "8 series" drops contain nitrogen compounds mostly.

Besides the fact that rain drops contain salt particles derived from the spray of sea water it has also been noticed that rain water brings down with it appreciable quantities of nitrites and nitrates. Recently Dhar and Atma Ram (J. Indian Chem. Soc. 10, 125, 1933) have estimated the amount of nitric nitrogen and ammoniacal nitrogen in Allahabad and Dehra Dun and found that appreciable amounts of these substances are brought down during rain ; the ratio of nitric to ammoniacal nitrogen was found to be greater than unity. In their paper they have also given a summary of the results of similar estimations carried out in other parts of the world. Their results are summarised below:—

(1) At Allahabad the average amount of ammoniacal nitrogen is 0·31 part in million parts of water and of nitric nitrogen 0·9 part in the same volume of rain water, the ratio of nitric to ammoniacal nitrogen being 2·9.

(2) From the summary of the analysis of rain water carried

out in various countries, it appears that the ratio of nitric to ammoniacal nitrogen is greater in tropical than in temperate countries.

Owens (Q. J. Roy. Met. Soc., 58, 282, 1932) has found presence of crystals, pollen and amorphous dust in country air, the crystals being those of sulphates, chlorides and nitrates of some alkalies and alkaline earths.

EFFECT OF SUSPENDED PARTICLES ON THE TRANSPARENCY OF THE ATMOSPHERE

As soon as condensation of water vapour takes place on the nuclei, a change in the visibility (distance upto which objects can be seen) of the atmosphere takes place. A quantitative idea of these changes can be had by means of visibility finder designed by Wigand (Meteorol. Zeit., S. 342, 1919 ; S. 216, 1924) or by the measurement of sun's radiation as done by Linke (Beitr. z. Physik. der frein Atmosphäre, 10, 91, 1922). W. Milch (Meteorol. Zeit., S. 109, 1924) has shown that the transparency of the atmosphere varies according to the origin of the air mass. In fact this transmission coefficient is now also utilised by the Norwegian Meteorologists for identifying air masses.

ELECTRIC CHARGE ON RAIN DROPS AND ITS CAUSES

The fog and cloud droplets carry charge and the efforts to dissipate fog or produce rain are wholly based on this property of fog and cloud. Wigand and Wittenbecher (Phys. Zeit., 27, 803, 1926) have measured the charge on fog drops and found high values of 350 to 2000 elementary charges per drop for anticyclonic radiation fog and 60 to 400 for cyclonic fog. The presence of both positive and negative charge was detected, the proportion of positively and negatively charged drops varying under different situations.

About the charge on rain drops and snow particles a reference may be made to classical experiments of Simpson (Mem. Indian Meteorol. Dept., 20, part 8, 1910) which were carried out in Simla during 1908 to 1909. Some of his results are given below:—

(1) The total quantity of positive electricity brought down by the rain was 3·2 times greater than the total quantity of negative electricity.

(2) Treating charged rain as equivalent to a vertical current of electricity, the current densities were, generally, smaller than 4×10^{-15} amperes per cm^2 ; but on a few occasions, greater current densities, both positive and negative were recorded.

(3) The charge carried by the rain was, generally, less than 6 E.S.U. per c.c. of water, but larger charges were occasionally

recorded ; in one exceptional thunderstorm of 13th May, 1908, the negative charge exceeded 19 E.S.U. per c.c.

(4) With all rates of rainfall positively charged rain occurred more frequently than negatively charged rain and the relative frequency of positively charged rain increased rapidly with increased rate of rainfall. With rainfall of less than about 1 millimetre in 2 minutes, positively charged rain occurred twice as often as negatively charged rain, while with greater intensities it occurred fourteen times as often.

(5) When the rain was falling at a less rate than about 0·6 millimetre in 2 minutes, the charge per c.c. of water decreased as the intensity of rain increased. With rainfall of greater intensity than about 0·6 millimetre in 2 minutes the positive charge carried per c.c. of water was independent of the rate of rainfall, while the negative charge carried decreased as the rate of rainfall increased.

(6) The data do not suggest that the negative electricity occurs more frequently during any particular period of a storm than during any other.

(7) More positive than negative electricity is brought down by snow in the proportion of about 3·6 to 1.

Thora C. Marwick (J. Roy. Met. Soc., 56, 39, 1930) has measured the electric charge on drops in different types of rain at Otago in New Zealand and observed that there is 94·6% positive charge in thunderstorm rain, 79·5% positive charge in ordinary rain, 100% positive charge in drizzle, and 39·4% positive charge in hail and rain. For snow equal amounts of positive and negative electricity were found, but charge per c.c. was found to be much greater for positive samples. For thunderstorms the greatest changes of potential gradient and highest charges occurred at the beginning of the storm.

Scrase (Met. Office, Geophys. Mem. No. 58, 1933) has found that 70% of dense fogs contain drops carrying negative charges of the order of 35 E.S.U.

Dauzére (Comptes Rendus, 189, 1092, 1929) has suggested that ice crystals in cirrus are positively charged due to action of ultra-violet light.

The causes responsible for the electrification of water droplets may be:—

(1) Adsorption of ions from the atmosphere.

(2) Breaking up of large drops by the resistance of the air through which they are falling at high velocity.

(3) Action of ultra-violet light in the upper air.

(4) Friction between water drops and ice crystals or dust particles.

(5) Collision between large and small drops.

We shall consider here the influence of the first two factors somewhat in detail as they have a direct bearing on the two rival theories of electricity in thunderclouds.

In Wilson's (J. Franklin Inst., 208, 1, 1929 in which a review of the theory is given) induction theory, which was originally suggested in another form by Elster and Geitel (Wied. Ann. 25, 116, 1883), each drop acquires by induction a negative charge above and a positive below, the normal electric field in the air being downward. As it falls through the air, or as the air blows past it, negative ions in the air will be attracted towards the lower parts of the drops and some will strike them and coalesce with them. The mobility of the positive ions in the air is considered to be too small for them to catch up the falling drops. Thus the drop will become negatively charged and the air will be left with a resultant positive charge. On this view the top of thundercloud should be positive and the bottom negative. This theory has been supported by observations on polarity of clouds by Wilson himself (Proc. Roy. Soc., 92, 555, 1916; Phil. Trans., 221, 73, 1921) and by Schonland (Proc. Roy. Soc., 114, 229, 1927; 118, 233, 252, 1928; also see Appleton, Watt and Herd, ibid., 111, 615, 1926; Wormell, ibid., 127, 567, 1930; Halliday, ibid., 138, 205, 1932; Gott, ibid., 142, 248, 1933).

Kähler (Gerlands Beitr. z. Geophysik, 27, 226, 1930) has counted at Potsdam Observatory the number of ions of various kinds, from the very mobile ions to the large slow ions, during light rain, heavy rain, squalls and thunderstorms and found that the results support Wilson's theory. Deppermann (Terr. Mag, 37, 179, 1932) and Sil (ibid., 38, 66, 1933) observed that the overhead false cirrus increased the intensity of normal electric field to a considerable extent and this also agrees well with the disruption theory of Wilson (Phil. Trans., 221, 105, 1921), false cirrus being a part of the upper part of cumulo-nimbus which may be positively charged.

From a study of the behaviour of a water drop in an intense electric field such as exists in a thunderstorm, J. J. Nolan (Nature, 132, 938, 1933) has come to the conclusion that the low mobility ions required by Wilson's theory of thunderstorm electrification are not directly produced by discharge from rain drops. The condensation nuclei of the ordinary type are also not produced by a discharge in an intense electric field (Nolan and Ryan, Ger. Beiträge zur Geophysik, 41, 185, 1934). If therefore the small ions produced copiously

by the discharge are to be loaded up so that they may be carried by an air current against an adverse field, the loading must be accomplished by attachment to some kind of body other than nuclei produced by the discharge itself.

Lenard (Wied. Ann., 44, 584, 1892) found that when a drop of pure water splashes against a plate the drop gets positively charged and the surrounding air is negatively electrified. Simpson's (Phil. Trans., 209, 374, 1909; Proc. Roy. Soc., 114, 376, 1927) theory is based on this Lenard effect. According to him thunderstorms are caused by the splitting of rain drops in an ascending current of air when they grow to more than a certain size. Electrification by splashing occurs and the negative electricity is carried upwards by the air of fine spray while the positive charge remains on the drop which is supported by the up-current. Thus the upper part of the cloud is negatively charged and the lower part positively, though Simpson considers that the negative electricity may be carried down again at the back of the cloud. This theory is completely supported by Simpson's observations on charge on rain drops at Simla (loc. cit.).

The measurements of Banerji (J. Roy. Met. Soc., 56, 305, 1930; Phil. Trans., 231, 1, 1932) about polarity of thunderclouds at Bombay have shown that the front part of thundercloud is negatively charged, the centre positively charged and the rear negatively charged. The results support Simpson's breaking-drop theory.

Observations of positive polarity of thunderclouds (positive above and negative down) recorded by Wilson and others (loc. cit.) fit in with breaking-drop theory, as shown by Simpson (Proc. Roy. Soc., 114, 376, 1927), if it is realised that a lightning discharge may start downwards from the lower, or positive, pole without reaching the ground.

Regarding production of electricity by spraying, Lord Kelvin (Proc. Roy. Soc., 57, 335, 1894; Phil. Trans., 191, 187, 1898) has shown that air bubbled through pure water carried with it a negative charge, but on the addition of salts of acids to water not only the charge diminishes but in some cases the sign of electrification may also reverse (also see Lenard, Wied. Ann. 46, 584, 1892). It has been shown before that the analysis of rain water reveals that it contains $NaCl$, $MgCl_2$, $MgSO_4$, $CaSO_4$ as well as nitrites and nitrates of ammonia. If this be the case it is possible that breaking of rain drops containing salt in solution will give negative charge to drops and positive charge to atmosphere. Under such circumstances the lower part of thundercloud may be negatively charged and the upper part positively charged—the same type of polarity as may be expected

according to Wilson's theory. D. Nukiyama and H. Noto (Japanese J. of Astro. and Geophys., 6, 71, 1928) from a study of charges on thunderclouds have concluded that the thunderclouds generated in the inland parts of Japan are of the Simpson type, while those generated near the coast are of the Wilson type. It is quite possible that near the coast there will be a considerable amount of salt nuclei available for condensation and as stated above, the breaking of such rain drops may give negative charge to the lower portion of the thundercloud and positive charge to the upper portion. Before, however, anything can be said definitely on this point, it is necessary that in such cases of polarity of thunderclouds, an analysis of rain drops is made to find out the salt concentration per drop in order to see whether it agrees with laboratory experiments.

INFLUENCE OF SUSPENDED PARTICLES IN THE ATMOSPHERE ON ITS ELECTRICAL CONDUCTIVITY AND ON THE VERTICAL POTENTIAL GRADIENT

Normally the surface of the earth is negatively charged and the air positively charged and the value of the vertical potential gradient is about 100 volts per metre. As a result of this vertical electrical field, positively charged ions, dust particles and water droplets move down while negatively charged particles move upwards. The electrical conductivity of the air at any point will thus depend upon the number of such charged particles present, the rate at which they move under the existing vertical field and the charge that is carried by each of them. As stated before, the small ions move fastest while the large ions consisting of dust particles, water droplets, etc., to which a small ion might have become attached move with only about one-threethousandth of the velocity of the small ions. Most of the current will thus be carried by the small ions as a result of their speed, although their number may be smaller than that of big ions. The number of small ions in the atmosphere may decrease considerably by combination with dust particles and water droplets and the conductivity may thus appreciably decrease. Light clouds, fog and mist diminish the conductivity of the air as a result of the adsorption of the ions ; the vertical potential gradient within the cloud may increase much and that in the air above and below the cloud diminish. A very thick cloud layer may reduce the vertical current, and hence the potential gradient at the ground almost to zero. Cumulus clouds as well as cirrus and other high clouds do not appreciably affect the potential gradient at the ground level. During rain or when a thundercloud passes overhead the potential gradient may considerably increase and it may even be reversed sometimes,

Very low or negative values of potential gradient in fine weather are generally associated with great dustiness of the air, sometimes the normal field may even increase due to dust if the particles are negatively charged, thus increasing the positive charge of the air. The potential gradient in higher levels (at a height of a few Kms.) is considerably reduced due to absence of dust particles.

Simultaneous measurements of electrical potential gradient of the atmosphere and different meteorological elements under different types of weather situations are very few. Recently Sil (J. Roy. Met. Soc., 59, 23, 1933) has studied variations in potential gradient at Poona caused by some meteorological phenomena and obtained very interesting results. In order to interpret such data it is, however, necessary that simultaneous measurements are also made of conductivity, the small and big ions and the dust and other particles as well along with potential gradient measurements ; it is also necessary to determine the chemical composition of dust and other particles. A summary of his results is given below :—

(1) During strong insolation the earth's field is weakened.

(2) On a dry hot day strong and gusty winds reduce the field to zero or even to negative values.

(3) The sea breeze reverses the normal field.

(4) During a dust-storm the earth's field is quickly reversed and a strong negative potential gradient established.

(5) During haze and fog the earth's field is increased, the effect being more marked with haze than with fog. When the fog begins to be lifted the potential suddenly decreases and sometimes is even reversed.

(6) When alto-cumulus and cumulus clouds formed overhead the potential gradient increased considerably.

Potential gradient variation over land is largely governed by variation of dust and nuclei ; generally the less the atmospheric pollution, the lower the potential gradient (Whipple, Q. J. Roy. Met. Soc., 55, 351, 1929). Chree (Proc. Roy. Soc., 95, 210, 1918) showed that good visibility went with low potential gradient and poor visibility with high potential gradient. Chree and Watson (ibid., 105, 311, 1924) have observed a close parallelism between daily variation of potential gradient and of pollution. The potential gradient variation curve shows two minima and two maxima in 24 hours. Hogg (Gerl. Beiträge zur Geophysik, 41, 1, 1934) has come to the conclusion that changes of the rate of ionisation and nucleus concentration determine the daily march of the conductivity of air.

STABILITY AND SETTLING OF CLOUD AND FOG AND FORMATION OF PRECIPITATION

The causes for the floating of cloud become clear if one considers the magnitude of drops in the cloud. W. Schmidt (Meteorol. Zeit. S. 183, 1909) has worked out the rate of fall of drops of various magnitudes and found that when $r = 0{\cdot}02$ cm. the descending velocity v is 1·8 cm./sec.; the expression changes over to Stokes-Kirchoff law for drops of smaller magnitude, when $r=5\times10^{-5}$, $v=3\times10^{-3}$ cm./sec. Thus it becomes clear that with the ordinary movements which take place in the atmosphere there will not be any difficulty in keeping the water drops in clouds suspended in the air. Also the drops being very fine the surface area is extremely large and hence adsorption can take place to a very appreciable extent ; the surface coatings so formed may increase the stability of drops.

If there was no horizontal or upward movement in the atmosphere the suspended particles would slowly settle due to action of gravity, the largest ones being in the lowest levels. Such conditions, however, do not persist and therefore the self-purification process of the atmosphere cannot take place to any appreciable extent except in the case of very large particles which are raised up during sand or dust-storms.

Fog and smoke particles in the atmosphere settle quicker under the action of gravity than particles of the same size and under the same density difference suspended in water. Fog drops consisting of water and of radius $400\mu\mu$ reach a falling velocity of 0·03 cm./sec.
(H. Freundlich, Kapillarchemie, 1922, S. 1083).

Smoke particles have a greater amplitude of Brownian movement than particles in liquid sols and thus the smoke particles will be prevented from settling rapidly. Cloud and fog particles, however, do not show any Brownian movement and therefore they will settle in air unless vertical convection currents prevent their fall.

If the particles of an aerosol diffuse the chances of collision increase and this may lead to flocculation of the particles. Diffusion as a result of Brownian movement is most pronounced with very fine particles and becomes less and less marked as the particles increase in size. The particles of a freshly formed smoke whose diameter is of the order of 10^{-7} cm. show a vigorous Brownian movement and the small as well as big ions which are also of this magnitude show a pronounced Brownian movement and diffusion. The work of Whytlaw-Gray and collaborators (Proc. Roy. Soc., 102, 600, 615, 1923) on smokes has shown that there are three distinct periods in the life history of such systems, *viz.*,

(1) An unstable period, lasting for five hours or more, in which the decrease in the number of particles with time is very rapid. This is due to aggregation of primary particles.

(2) A stable period in which the number of particles decreases very slowly, chiefly as a result of sedimentation. This stage may last for 24 hours or more.

(3) Stages (1) and (2) overlap to produce intermediate stage in which both aggregation and settling take place.

As the particles decrease, the frequency of collision will also decrease and when the particles reach a radius of the order of about 10^{-5} cm. or more the Brownian movement is found to be almost absent; the particles under such circumstances settle under the action of gravity, flocculation being absent. The photographs of zinc oxide taken by Whytlaw-Gray, (loc. cit.) also show that there is a tendency for larger particles to grow at the expense of smaller particles instead of particles of the same size combining with each other.

Although clouds and fog may not flocculate as a result of diffusion, it being small or negligible, they may do so as a result of neutralisation of their electric charge or by the removal of the film of absorbed gas which may surround the drops. The latter can be removed by charging the drops, the effect of charge being to oppose the effect of surface tension (Burton and Wiegand, Phil. Mag., 23, 150, 1912). It is found that water drops colliding in air rebound from each other as a result of the surrounding film of gas but if the air in the immediate vicinity is charged, the drops become charged due to adsorption of ions and then coalesce when they collide with each other (Rayleigh, Proc. Roy. Soc., 28, 406, 1879; 29, 71, 1879; 34, 130, 1882). Even if some particles in an aerosol are neutral, flocculation can take place between charged particles and neutral particles, as a charge opposite to that on charged particles will be induced on neutral particles. In a cloud or fog generally some particles may be negatively charged while others may be positively charged and therefore flocculation is quite possible. The diffusion in such a system is small but there being always some turbulence in the atmosphere, the particles can come in contact with each other for allowing coalescence to take place. When the particles are all neutral a breeze may bring them together and larger aggregates may be formed. The particles in a fog or cloud can also grow as a result of evaporation of relatively smaller particles, or as a result of further condensation from vapour phase as a result of cooling of the system.

In the case of condensation of zinc vapour in various gases Kohlschütter (Kolloid Zeit., 42, 209, 1927; also Schmauss, Meteorol. Zeit. S. 473, 1927) has also shown that under the same conditions of

pressure and temperature the size of the particles increases and their number decreases with a decrease in the density of the gas ; with the same gas an increase of pressure increases the degree of dispersion as well as the number of particles. Schmauss and Wigand (loc. cit. S. 16) consider that such an effect is produced in the atmosphere when a cloud is lifted up ; decrease of pressure may probably explain the decrease in the degree of dispersion. Kopp's observations (loc. cit.) also show that in a thundercloud the drops at the bottom are finer while those higher up are bigger and fewer in number. Kopp's observations can, however, be also explained on the view that the number of nuclei in higher levels being small relatively large drops will be formed.

If the cloud or fog contains particles of unequal size it may become unstable due to growth of relative larger particles at the expense of smaller ones as a result of isothermal distillation. If all the particles are however of the same size the stability will not be affected as a result of this evaporation effect.

In the case of a town fog the stability of which is sometimes very great, there are other factors to be considered. The evaporation of the fog particles might be prevented as a result of the absorbed layer of organic gases as well as oil at the surface.

Recently A. Wigand and E. Frankenberger (Phys. Zeit., 31, 204, 1930) have given a theoretical treatment of the question of persistence and coagulation of fog and cloud by considering the effect of the electric double layer and the application of v. Smoluchowski's theory of kinetics of coagulation of hydrosols. It must be stated here that even at present our understanding of the property of the double layer round the particles in a hydrosol is not quite clear and complete, and we are not at all sure of the existence of double layer in the case of charged particles in fogs and clouds. Even granting the existence of double layer round the particles in clouds and fogs, we are not aware, if in the case of clouds and fogs also as in the case of hydrosols, the charge on the particles has to be reduced to a particular value before coagulation of clouds and fogs can take place. It is known that rain drops carry electric charge; if it is so, the case is somewhat different from that of hydrosols unless one assumes that the rain drops have got re-electrified after leaving the cloud as a result of adsorption of ions ; there is however no conclusive experimental evidence for or against this assumption. Also it is doubtful if the coagulation process is such a simple reaction as postulated by v. Smoluchowski ; in the case of hydrosols there is definite evidence that the coagulation reaction has an auto-catalytic character. During the first period after the addition of electrolyte the alteration in the

sol is slight ; then after some time, the amount flocculated increases rapidly and finally it slowly approaches the end state. There is no experimental evidence to show whether in the case of clouds and fogs the aggregation is of the simple type as postulated by v. Smoluchowski or has an auto-catalytic character. It is doubtful whether the results of Defant and Köhler about the drop series of the order of 1, 2, 4, 8, etc., can be taken to indicate coagulation of droplets in a cloud or fog similar to that in the case of hydrosols. The theoretical treatment given to the question of coagulation in clouds and fogs by Wigand and Frankenberger should therefore be taken with reservations.

On examining critically various theories which hold for the coagulation of suspended matter in hydrosols, it is found that these fail to explain satisfactorily the precipitation of rain from clouds. Almost all the rainfall over the world occurs in connection with the movements of "lows" and "heat thunderstorms". In these cases warm and moist air is made to rise higher up. In the case of warm front rain the warm moist air rises over relatively cold dry air. The cold front rain is as a result of the lifting of warm moist air by cold dry air. In the case of heat thunderstorms warm moist air is made to rise as a result of strong convection set up due to insolation. Thus rain always forms in an ascending air current. Its mechanism can therefore be pictured as follows :—

As the warm moist air rises up, its temperature begins to fall and when the dew point is reached condensation begins to take place on nuclei which are always present in large numbers ; condensation may begin even before dew point is reached if the nuclei are very hygroscopic. Now as the air continues to rise further, the cloud particles already formed may lag behind and the air is thus made gradually poorer and poorer in nuclei. Therefore a higher degree of supersaturation will be necessary before condensation can take place ; the number of nuclei left in the rising air mass being comparatively very few, the drops formed as a result of further condensation will be sufficiently large and fall to give rain. It is possible that these drops may further grow during their fall through ascending air current as a result of more moisture condensing upon them because of their lower temperature than the surrounding air or due to coalescence on account of collision with droplets that may be oppositely charged or similarly charged but having a different density of charge. The nature of precipitation—drizzle, heavy rain, etc.,—will depend upon the amount of moisture available as well as the conditions of condensation.

About the nature of precipitation Schmauss (Meteorol. Zeit., S. 339, 1927) has mentioned that the centre of Munich gets excess of

weaker rain than the adjoining suburbs (smaller drops in the middle of the town than in the surrounding area). This he considers due to the fact that in the heart of the town a considerably large number of nuclei are present due to working of factories, and therefore relatively smaller drops are formed, the amount of water vapour available for condensation being the same in the two cases. Of course it is a common observation that the frequency of the low clouds and fogs is greater over an industrial area than over the adjoining countryside. This is due to a considerable number of nuclei that are made available from the chimney smoke, some of the nuclei being very hygroscopic. Condensation can therefore occur even if air is unsaturated. Moreover with the chimney smoke, some water vapour also escapes—in fact this is the result in almost every combustion process—and thus the amount of water vapour available for condensation is also relatively great. The same causes may also be responsible for cloud formation over the mouths of active volcanoes.

In this connection mention may also be made about a recent paper by Ashworth (J. Roy. Met. Soc., 55, 341, 1929; also see Nature, 132, 443, 1933) in which the influence of smoke and hot gases on the rainfall is considered. He has analysed the records of a number of years of Rochdale, an industrial town in England, and shown that (1) a smaller average total rainfall occurs on Sundays than on other days, (2) during working hours 7 A.M. to 6 P.M., the duration of rainfall was greater than for other part of the day and (3) there was a close agreement between the amount of impurity and rainfall. He ascribes this effect to the smaller number of nuclei in the atmosphere on Sundays due to factories being closed, and the larger number of condensation nuclei available in smoke and hot chimney gases during working hours. It may be pointed out here that such an analysis by Mr. U. N. Ghosh for Ahmedabad, a large industrial town in Gujarat, did not show relation of the type observed by Ashworth in the case of Rochdale; analysis showed that the average total rainfall on Sundays was larger than on other days, the ratio of the total rainfall on all Sundays during last 31 years×7 to that of the total of all the days being 1·09. On the other hand, for Asansol, in the middle of a coal district in Bengal, the value of the ratio is 0·93 (average of 31 years), and for Cawnpore, another industrial town in the East United Provinces, the value of the ratio is 0·87 (average of 31 years). The results for Asansol and Cawnpore apparently support Ashworth's analysis for Rochdale, Halifax and Llanfairfechan, the values of the ratio at the last three stations being 0·94, 0·98 and 0·93 respectively (Ashworth, Nature, loc. cit.). It will be also interesting to mention here the results of similar ana-

lysis for Deesa, a city in Gujarat in the Palanpur State, in which there is hardly any factory; the value of the ratio comes to 0·93 (average of 31 years). It is difficult to understand the reason for less average rainfall on Sundays than on other days at Deesa; one might incline to the view that condensation nuclei are not the deciding factors for these differences of rainfall on Sundays and other days.

In the end I wish to thank Dr. S. Mal for the help in preparing this article and Dr. K. R. Ramanathan for some valuable suggestions.

THE SPATIAL CONFIGURATION OF CYCLOHEXANE AND ITS DERIVATIVES

BY

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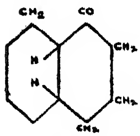
During the past few years, a large amount of work has been done on the stereoisomerism of homo- as well as hetero- dicyclic systems, and results of considerable interest have been obtained. Thus Hückel and his co-workers (Hückel, Nach, Ges, Wiss. Gottingen 1923, 43 ; Annalen 1925, *441*, I ; 1926, *451*, 109 ; Hückel and Friedrich, ibid., 1926, *451*, 132 ; Hückel and Stepf, ibid., 1927, *453*, 163, etc.), have shown that of α-decalone, (Ia and Ib), β-decalone (IIa and IIb), and hexahydro-β-hydrindone (IIIa and IIIb), each exists in two isomeric forms.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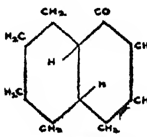
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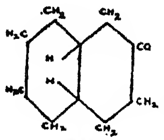
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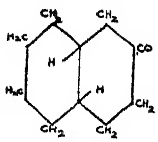
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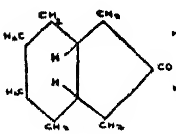
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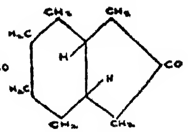
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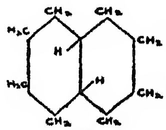
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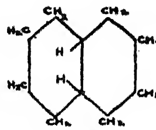
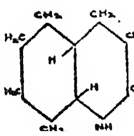
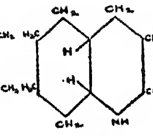
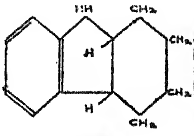
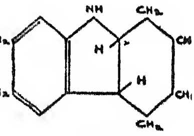

IV(b)

Similar cases of isomerism have been reported by the same authors in the case of decahydro-α-naphthol, decahydro-β-naphthol, hexahydro-α-hydrindol and hexahydro-β-hydrindol and Willstatter and Seitz (Ber. 1924, *57*, 653) have obtained two isomeric decahydro-naphthalenes (IVa and IVb). In the case of hetero-bicyclic compounds, Hückel and Stepf (Loc. cit.) have isolated two isomeric decahydroquinolines (Va and Vb) while the isolation of two forms of hexahydro-carbazole (VIa and VIb) by Gurney, Perkin and Plant (J. C. S. 1927, 2676) furnishes the example of such isomerism in hetero-tricyclic systems.


V(a)

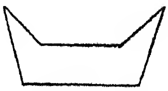

V(b)


VI(a)


VI(b)

The isomerism of the above-mentioned compounds can be easily explained on Mohr's views of fused rings (J. Pr. Chem. 1918, *98*, 315). According to him, the fusion of a cyclohexane ring with cyclohexane and cyclopentane rings forming decahydronaphthalene and hexahydrohydrindene can take place by the linking of either the *cis* or *trans* valencies. The resulting dicyclic systems have been proved to be free from strain and hence multiplanar (Rao, J. C. S., 1930, 1162 ; Kandiah, J. C. S. 1931, 952).

This brings us to the cognate question of the spatial configuration of the cyclohexane ring. On the basis of Baeyer's Strain Theory, the cyclohexane ring has an intracyclic angle of 120°, and as the normal carbon tetrahedral angle is 109·5°, the valencies of carbon have been deflected from their normal path through 5·25°. Thus there is a fairly good amount of strain in the cyclohexane ring. According to Sachse (Ber. 1890, *23*, 1363) the strain in cyclohexane is eliminated by the assumption of a multiplanar form, and this can be easily seen by building up the model of this ring. The same author has pointed out that two strainless and hence multiplanar modifications of cyclohexane are possible, *e.g.*, the boat and the arm-chair forms (VIIa and VIIb). In this connection, it is interesting to study the mathematical proof given recently by Gunjikar (Jour. Univ. Bombay. Vol. II Part II page 7).


VII(a)

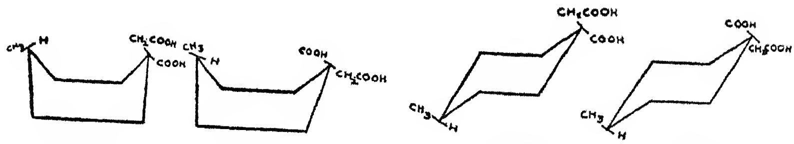

VII(b)

The experimental deductions demanded by Sachse's strainless forms of cyclohexane have not, so far, been experimentally realised. Numerous attempts which were made to isolate two forms of cyclohexane or its simple mono-substitution products failed (Wightman J. C. S. 1925, *127*, 1421 ; 1926, *129*, 2541). Werner and Conrad (Ber. 1899, *32*, 3046) unsuccessfully attempted the resolution of cis-hexahydrophthalic acid into its optically active forms. In course of their attempts to reduce the isomeric xylenes by hydrogen, in presence of various metallic catalysts, Chavanne and Becker (Bull. Soc. Chim. Belg. 1922, *31*, 95) observed the formation of two different dimethylcyclohexanes, in the case of O-xylene, by using nickel and platinum

as catalysts ; but this isomerism could be equally explained on the assumption of the uniplanar structure of cyclohexane. The same explanation would also be sufficient to explain the existence of two isomeric forms of hexahydro-p-toluic acid (Einhorn and Willstatter, Annalen 1894, *280*, 160).

The failure to isolate the isomeric forms of cyclohexane as well as its monosubstitution derivatives are due to the fact that the strain involved in the conversion of the boat into the arm-chair type is very small and that this change is continuously going on through the intermediate, uniplanar form. This being the case, these derivatives are too labile for isolation. From the X-Ray examination of the crystal structure of benzene hexahalides, Hendricks and Bilicke (J. Amer. Chem. Soc. 1926, *48*, 3007) came to the conclusion that the spatial arrangement of the atoms in cyclohexane is more complex than is suggested by the simple tetrahedral models. On the other hand Hassel (Zeit. Electro-chem. 1931, *37*, 540) concluded that the cyclohexane ring was strainless, after studying the X-Ray crystal-structure of 1 : 4-dibromo and 1 : 4-diiodo-cyclohexanes. Thus the evidence from the X-Ray examination of the crystal-structure of cyclohexane derivatives is conflicting.

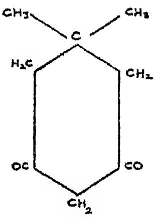
We have already referred to the fact that the reason of failure to isolate the stereoisomers demanded by the strainless forms is due to their lability. If this is overcome by the introduction of certain substituents, the vibrations will be damped with the result that stability will be conferred upon certain isomers. Acting on this reasoning, Qudrat-i-Khuda (J. Ind. Chem. Soc. 1931, 8, 277) isolated four different forms of 4-methylcyclohexane-1-carboxy-1-acetic acid (VIIIa, VIIIb, VIIIc, VIIId). This is the first instance of the isolation of four theoretically possible isomers in the cyclohexane series. This work has been criticised by Prof. Thorpe (J. C. S. 1931, 1023) on the grounds that the four isomeric acids have not been degraded to a common simple substance, and that as 4-methylcyclohexanone is usually liable to contain 2-methylcyclohexanone as an impurity, the acids obtained in small amounts may be traced to the extraneous sources. This criticism of Prof. Thorpe has remained unanswered so far.

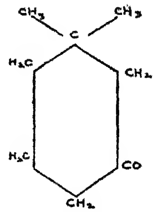


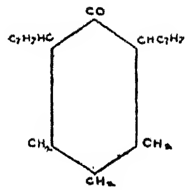
VIIIA *VIIIB* *VIIIC* *VIIID*

By reducing dimethyl-dihydroresorcinol (IX) by Clemmenson's method, Qudrat-i-Khuda (Nature, 1933, *32*, 210) isolated 1 : 1-dime-

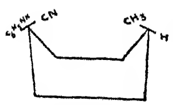
thyl-cyclo-hexan-3-one (X), while an isomeric ketone was formerly prepared by Clossley and Renouf (J. C. S. 1907, 73) by first treating the same dihydroresorcinol (IX) with phosphorous trichloride, and reducing the resulting chloro-derivative with sodium and moist ether. The existence of these two isomeric ketones (X) can be explained only on the multiplanar configuration of the cyclohexane ring. Very recently Cornubert and M. De Demo (Comp. Rend. 1933, *197*, 1656) have announced the possible existence of three isomeric 2 : 6-dibenzyl-cyclohexanones (XI).

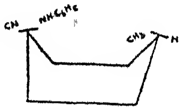

IX

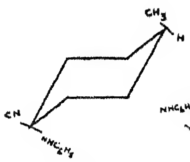

X

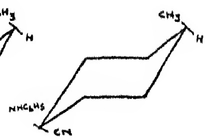

XI

In view of the great theoretical interest attached to this subject, we have been doing some work on certain trisubstituted derivatives of cyclohexane in these laboratories. With the object of isolating the isomeric derivatives of the strainless forms of cyclohexane, we have condensed a number of aromatic amines with the cyanohydrins of cyclohexanone and isomeric methylcyclohexanones. 4-methylcyclo-hexanone-cyanohydrin and aniline will give rise to the four stereoiso-meric compounds represented by XIIa, XIIb, XIIc, XIId. The iso-lation of these isomers and preparation of their derivatives are beset with great practical difficulties, but certain interesting results have been obtained with 4-methyl-cyclohexanone and we are following up this enquiry.


XII(a)

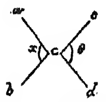

XII(b)


XII(c)


XII (d)

Reverting to the original question of the uniplanar character of cyclohexane, most of the reasons given so far have been mainly of the negative character. The fact that cis- and trans -decalin are strainless and multiplanar does not mean that their components are also strainless in a free condition. As the two strainless forms of cyclohexane are easily interconvertible, it is just possible that in all the chemical reactions, this ring is behaving as a strained and uni-planar ring which is the intermediate stage in passing from one form

to the other. With the exception of a limited number of doubtful cases, all the isomers encountered so far, are easily explicable on the uniplanar configuration of cyclohexane. Moreover, during the recent years Thorpe, Ingold and their collaborators (Beesly, Ingold and Thorpe J. C. S. 1915,*107*, 1080 ; Ingold and Thorpe, ibid., 1928, 1320, *etc.*), have applied the *valency-deflexion* hypothesis to show the condition of strain in this ring. A brief reference to this hypothesis is necessary in order to show its bearing on the question under discussion. It assumes that when a normal angle between the two valencies *a* and *b* of a carbon atom is changed either through their inclusion in a ring complex or their attachment to heavy groups, the angle between the remaining valencies *c* and *d* undergoes a corresponding change in the opposite direction. Thus if the angle *x* becomes greater than the normal angle 109·5°, the angle θ will be smaller than this amount, with the result the groups attached to the valencies *c* and *d* will converge to each other.



The experimental support to this hypothesis has been given by the formation and stability of Spiro-compounds by the removal of HBr from the two acetic acid residues of β-β-disubstituted glutaric acids as follows.

Table I shows that as the value of θ decreases, the stability of spiro-acids increases.

TABLE I.

R R_1	Angle θ	Stability of the spiro-acids.
Me, Me	109·5°	Rapidly decomposed by 5% HCl at 200°.
Cyclopentane	109·7°	Rapidly decomposed by 5% HCl at 200°.
Cyclohexane	107·2°	Unaltered by Conc. HCl at 240°.
Cycloheptane (strainless)	109·5°-y (where y is small)	Decomposed by 20% HCl at 240°.
Trans-decalin	109·5-y (where y is small)	Decomposed by 10% HCl at 240°.

(cf. The Annual Reports of the Chemical Society, 1930, page 155.)

But the most important evidence brought forward by Thorpe and his co-workers was the study of the tautomerism of various α-keto-β·β-disubstituted glutaric acids to the isomeric hydroxy-ring acids in presence of 64% potash. It was definitely shown that the percentage of the ring hydroxy acid in the equilibrium mixture increased as the angle θ decreased.

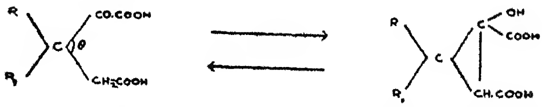
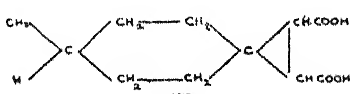


Table II shows the relation between angle θ and the percentage of ring hydroxy acid.

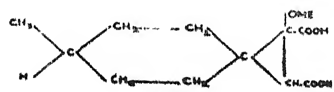
TABLE II.

RR_1	Angle θ	Percentage of ring hydroxy acid in equilibrium mixture.
2-hydrogen	115·3°	0
2-methyl	109·5°	0
Cyclopentane	109·3°	0
Methyl, Ethyl	....	0
2-ethyl	....	62
2-n-propyl	....	71
Cyclohexane	107·2°	100
Trans-decalin	109·5°-y (where y is small)	0

From the above two tables it is seen that the effect of the cyclohexane ring is different from that of trans-decalin and cyclopentane rings both of which are strainless. Hence the former must be possessed of a considerable amount of strain, and therefore uniplanar. When, however, the author studied the effect of methylcyclohexane ring on the carbon tetrahedral angle on the basis of the *valency-deflexion* hypothesis, it simulated the behaviour of strainless rings, like cyclopentane, and specially trans-decalin and hexahydro-hydrindene. Attempts were made to isolate the isomeric spiro-acids (XIII and XIV) demanded by this assumption without any success. (Desai, J. C. S. 1932, 1047).



XIII



XIV

To sum up, the present position of this vexed question is that despite the hypothetical existence of two multiplanar forms of cyclohexane, and its derivatives, the over-whelming chemical evidence is in favour of the uniplanar configuration, though it must be admitted that evidence is gradually accumulating to support the other view.

Summaries And Abstracts of Theses for the M. Sc. degrees.

1.—*Studies in the Chemistry of Imido-chlorides.* By R. C. SHAH and N. B. ITCHAPORIA, B.Sc. A summary of the thesis submitted by Mr. Itchaporia for the M.Sc. degree of the Bombay University. (September, 1933.) Royal Institute of Science.

PART I.—*Condensation of Benzanilide-imido-chloride with substituted Dialkylanilines with anhydrous aluminium chloride as condensing agent :* Synthesis of *Dialkyl aminobenzophenones.*

In continuation of the work of Shah and Chaubal (J. 1932, 650), Shah and Chaubal's new synthesis of dialkyl aminobenzophenones has been applied to the condensation of benzanilide imido-chloride with substituted dialkylanilines. It has further been improved upon by the use, in place of carbon disulphide, of dry ether, which has the unique property of readily dissolving anhydrous aluminium chloride.

The dialkylanilines used were dimethyl-o-, -m-, -p-toluidine, diethyl-o-toluidine, dimethyl-α-naphthylamine, methylbenzylaniline, and ethyl benzylaniline. The synthesis was successful in all the cases, the resulting ketones being obtained in good yields. The general applicability of the method is thus established.

All the ketones are new, and are expected to be of service as intermediates for the preparation of dyes and of synthetic drugs.

A number of characteristic derivatives of the ketones were prepared and interesting observations made regarding the influence of steric hindrance on the formation of the oximes and the methiodides.

Appendix (*a*). *Use of dry ether as solvent for anhydrous aluminium chloride in organic synthesis.*

Attention is directed to the potential value of the observation made during the course of the work that dry ether which readily dissolves anhydrous aluminium chloride, is the best solvent for the Shah and Chaubal's synthesis. Dry ether on account of this valuable property may advantageously replace the usual solvents, which do not dissolve aluminium chloride, in many of the Friedel-Craft's reactions.

Appendix (*b*). Some reactions of dimethyl aminobenzophenone

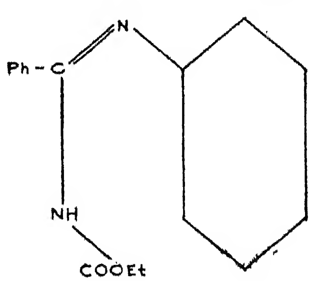
and the Beckmann transformation of its oxime. Several reactions of dimethylaminobenzophenone including nitration, bromination, and formation of the methiodide, have been studied.

The Beckmann transformation of the oxime carried out by means of phosphorous pentachloride in dry ether gives benzoyl dimethyl-p-phenylene diamine C_6H_5 CO. NH. $C_4H_4N(CH_3)_2$, which was definitely identified by direct comparison with an authentic specimen. This leads to the anti-configuration for the oxime.

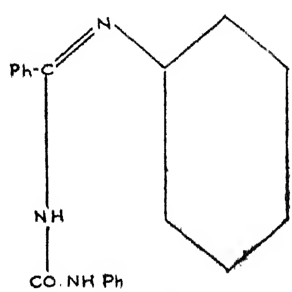
PART II.—*Condensation of Benzanilide-imido-chlorides with methanes: A new Synthesis of 2-phenyl-4-oxy-quinazolines.*

As part of a comprehensive study, having for its object the synthesis of heterocyclic nitrogen compounds from anilide-imido-chlorides, benzanilide-imido chlorides are condensed with sodium derivatives of methanes in ethereal medium.

Benzanilide-imido chloride when condensed with ethyl methane in the above manner gave phenyl iminobenzyl-ethyl-methane (I), which is an oil. Several reactions of this substance were studied including hydrolysis, bromination, action of amino compounds and the action of heat. The action of amino compounds gives high melting crystalline derivatives which serve to characterise the oily condensation product, *e.g.*, the action of aniline gives (II). The action of heat smoothly converts (I) into 2-phenyl-4-oxy quinazoline (III) of known constitution, by the elimination of a molecule of ethyl alcohol.



(I)



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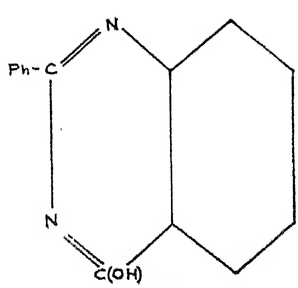


(III)

Methyl and acetyl methane similarly condense with benzanilide-imido-chloride to give phenyliminobenzyl-methyl methane and phenyl-imino-benzyl-acetyl methane which are converted by the action of heat into 2-phenyl-4-oxy-quinazoline and 2-phenyl-3-acetyl-4-oxy quinazoline respectively.

Benz α– and B-naphthanilide-imido-chlorides condense with ethyl methane giving α–naphthyliminobenzyl-ethyl methane and B-naphthyliminobenzyl ethyl methane, which on heating undergo ring closure with the formation of 2-phenyl-7 : 8-benzo-4-oxy quinazoline and 2-phenyl-5 : 6-benzo-4-oxy quinazoline, respectively, both of which are new.

The present work provides a new and useful synthesis of 2-phenyl-4-oxy-quinazolines.

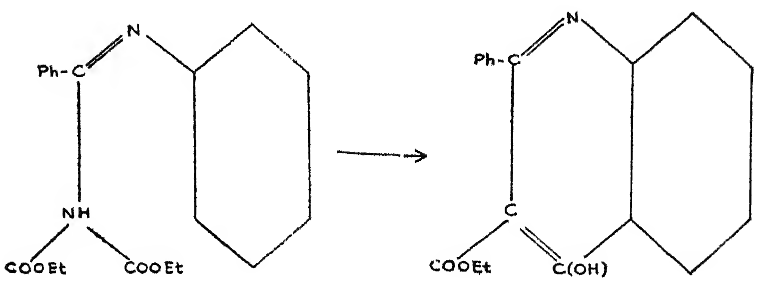
R. C. S.

II.—*"Syntheses in the Quinoline Series."* By R. C. SHAH and V. R. HEERAMANECK.—A summary of the thesis submitted by Mr. Heeramaneck for the M.Sc. degree of the Bombay University. (December, 1933). Royal Institute of Science.

PART I.—*Condensation of anilide-imido-chlorides with Ethyl sodium-malonate : Synthesis of 2-phenyl-4-hydroxy-3-carboxy quinolines.*

The condensation of benzanilide-imido-chloride with ethyl sodium-malonate was first studied by "Just" who made the interesting observation that the condensation product (I) was connected by the action of heat into ethyl 2-phenyl-4-hydroxy-quinoline - 3-carboxylate (II) ring closure taking place with the elimination of a molecule of alcohol. He also studied few other cases of this kind.

Just carried out the condensation by refluxing an ethereal solution of benzanilide-imido-chloride (1 mol.) with ethyl sodium-malonate (1 mol.). Seka and Feuchs (Monatsch, 1793T *57*, 52-



(I) (II)

62) have modified Just's method by carrying out the condensation in a sealed tube or in an autoclave at a high temperature.

The authors have substantially improved upon Just's method, by

using 2 mols of malonic ester instead of 1, which lessens the yield of the bye-product, *viz.*, the dicondensation product and carrying out the condensation in toluene instead of in ether.

Some new reactions of the typical monocondensation product [α-phenyl-iminobenzyl] -malonic acid and diethyl ester have been studied and new methods for the quinoline ring closure worked out.

In order to study the influence of substituents, the following imido chlorides were condensed by the author's modified method with ethyl sodium malonate :—p-nitrobenzanilide—, o-chlorobenzanilide—, benz-m-and p-nitranilide—, benz-o-, -m-, and p-toluidide—, benz-o-, m- and p-chloranilide—imido chlorides.

The condensation products were isolated in most cases in good yields in the crystalline condition, and further converted into quinoline derivatives by the action of heat. Most of the condensation products and the quinoline derivatives are new.

Imidochlorides derived from meta substituted anilines gave as expected a mixture of meta and ana substituted quinoline derivatives.

It is concluded, from the experimental results that the presence of the substituents has no appreciable influence on the condensation or on the subsequent quinoline ring closure, in most cases.

The author's modified method, which is obviously superior to Just's original method, or to Seka and Feuch's modified method, is well adapted as a general method for the synthesis of 2-phenyl-4-hydroxy-3-carboxy quinolines or 2-phenyl-4-hydroxy quinolines

PART II.—*The "Just" reaction* has been extended to the naphthalene series, and benz -α-, and-B-naphthanilide imido chlorides were condensed with ethyl sodio-malonate. The Condensation products were converted by heating into ethyl 2-phenyl-4-hydroxy-αnaphthoquinoline-3-carboxylate and ethyl 2-phenyl-4-hydroxy-β-naphtho - quinoline - 3-carboxylate, both of which are new.

PART III.—*Reaction of Ethyl 2-phenyl-4-hydroxy-quinoline - 3-carboxylate.*

Some reactions of the compound were studied in connection with the work described in Part I, since very little is known about its chemical behaviour.

The compound has been decarboxylated by a new method to give 2-phenyl-4 hydroxy-quinoline.

By the action of phosphorous pentachloride, ethyl 4-chloro-2-phenyl-quinoline 3 - carboxylate is obtained in good yield.

Alkylation by sodium ethoxide and ethyl iodide gave a C-ethyl derivative whose constitution follows from the fact that it is identical with the product obtained through the condensation of benzanilide-imido-chloride, and C-ethyl malonic ester.

The behaviour of 2-phenyl-4-quinoline-3-carboxylate towards ferric chloride and bromine definitely shows that the solid crystalline compound has the ketonic constitution of a dihydroquinolone.

R. C. S.

THE LATE DR. A. N. MELDRUM, D. Sc.

Obituary

Professor Andrew Norman Meldrum

By the death of Prof. A. N. Meldrum as a result of accident on the 12th of March, 1934, at Edinburgh, the University of Bombay has lost one of the pioneers, organisers and promoters of scientific education and chemical research in the presidency. He served on a large number of University Committees for many years, was an active member of the Senate and the Syndicate during 1922-1930 and was elected Dean of the Faculty of Science in 1930. As a member of the Visvesvaraya Committee he took a prominent part in drafting a scheme for founding the new Bombay University Department of Chemical Technology. In fact, his services are so well-known that everyone mourns his death with profound regret.

Prof. Meldrum was born in Alloa, Scotland, on March 19, 1876, and was educated first at Gordon's College, Aberdeen, and later at the Royal College of Science, London, where he obtained his A.R.C.Sc. in 1896. He then returned to Aberdeen and took his B.Sc. with first class honours in Chemistry and was Neil Arnott prizeman in Experimental Physics. Prof. Meldrum received his research training by working on problems of Organic Chemistry under the late Professor Francis Robert Japp, F.R.S., at Aberdeen. At this time he showed signs of doing more substantial service in another branch of science, namely, Historical Chemistry. Being a clear thinker, a sound experimenter and an impartial critic he found in Dalton's Atomic Theory a fascinating subject with an immense scope for further study and research. He then procured all available material from original sources and published an elaborate and thoughtful monograph on "Avogadro and Dalton : The Standing in Chemistry of their Hypotheses", for which the University of Aberdeen awarded him the D.Sc. degree in 1904. Prof. Japp remarks in the preface : "The view here stated as to the true ratiocinative order of the precedence of the molecular and atomic hypotheses has been held by various workers ; but I have nowhere else seen it expounded with such wealth of illustration and with so exhaustive a knowledge of the fundamental literature of the subject as in the present monograph by Dr. Meldrum."

Having received a research fellowship from the Carnegie Trust for the Universities of Scotland, Dr. Meldrum next proceeded to

Manchester and Sheffield to work on problems related to Organic and Physical Chemistry in collaboration with the late Prof. W. H. Perkin, Jun., and W. E. S. Turner respectively. Here he also synthesised independently β-lactonic acid and β- and γ-coccinic acids : substances related to cochenillic and carminic acids. Although actively engaged in Organic and Physical Chemistry research, Prof. Meldrum did not give up his pursuits in Historical Chemistry : on the contrary he worked in that branch more assiduously than before and contributed a valuable series of papers "On the Development of the Atomic Theory" to the Literary and Philosophical Society of Manchester. He also published the work of two Irish Chemists, Bryan Higgins and William Higgins in the *Reports* of the *British Association* and an account of Gay Lussac's Law, its centenary in *Nature.*

Dr. Meldrum taught Chemistry at the Universities of Liverpool, Manchester and Sheffield and at the time he got an appointment in the Indian Educational Service in 1912 he was assisting Prof. Japp at Aberdeen.

In India Dr. Meldrum joined the Madhavlal Ranchhodlal Science Institute, Gujarat College, Ahmedabad, as Professor of Science. He devoted all his time in the beginning to the equipment of the Science laboratories at the Institute and to improving the University Science courses. Being in an important industrial centre like Ahmedabad, he next attempted to popularise the study of science and bring about the happy blending of science and industry. As a nominated member of the Government he rendered useful service in the Ahmedabad Municipality.

From 1918-1922 Prof. Meldrum carried on research, in collaboration with his students, on condensations of chloral with gallic and cresotic acids, manufacture of casein, sulphonation of salicylic acid and related problems. In 1922 he was transferred as Professor of Organic Chemistry to the Royal Institute of Science, Bombay, where finding greater facilities for further research on the chemistry of chloral compounds, sulphonic acids, etc., he soon established a school of Organic Research. In 1925 he was appointed Principal of the Royal Institute of Science. Among the important results of his work on chloral condensations may be mentioned the syntheses of substituted phenylacetic acids and cochenillic acid, the colouring matter of cochineal. The latter was prepared by one of his pupils, the late Mr. K. S. Vaidyanathan.

Prof. Meldrum was a Trustee of the Prince of Wales Museum of Western India and a member of the Provincial Council for Agricultural Research. He was the President of the Chemistry Section

of the Indian Science Congress in 1923, an honorary Editor of the Journal of the Indian Chemical Society from 1925-26 and Vice-President of the same Society from 1927-29.

On the retirement of Prof. Meldrum in 1931 a memorial was raised in his honour and an annual prize known as the Meldrum Memorial Prize has now been founded at the Royal Institute of Science. Towards the end of his career in India and subsequent to his retirement in England Prof. Meldrum remained busy in making inquiries for an intensive study of the works of Lavoisier and Priestley. He published three lengthy papers dealing with Lavoisier's part in "The Eighteenth Century Revolution in Science", with his historic "Three Notes on Combustion : 1772," and with his "Early work in Science : 1763-1771". He also delivered one of the three commemorative addresses on Joseph Priestley before the Chemical Society in April 1933. Since last January he was engaged in a careful examination of literature pertaining to Black's discoveries but unfortunately the work remains incomplete since he met with a fatal accident on March 12. His only son died in 1933 and he is survived by his widow and two daughters.

Those who had the good fortune to study Chemistry, receive research training and serve under Prof. Meldrum would agree that he was a brilliant and painstaking teacher who always saw that the foundations of the subject in the student's mind were well and truly laid, a pleasant and amiable colleague and a just and sympathetic administrator. He had indefatigable industry, efficiency and patience. Besides in character he was as great as in scholarship. His simplicity was coupled with firmness and his invincible modesty had a dislike for publicity. These made an ever-lasting impression on the minds of those who had the pleasure of knowing him and the privilege of working with or under him. By his sad demise "the activities of one of the best informed writers on historical matters relating to the eighteenth and nineteenth century chemistry have come to a close".

The following is the list of research papers published by Prof. A. N. Meldrum either alone or in collaboration with others.

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2. Furfuran Derivatives from Benzoin and Phenols, by F. C. Japp and A. N. Meldrum, *ibid.*, 1899, *75*, 1035.

3. Interaction of Benzoin with Phenylenediamines, by F. C. Japp and A. N. Meldrum, *ibid.*, 1899, *75*, 1043.

4. Homologues of Anhydracetonebenzil, by F. C. Japp and A. N. Meldrum, *ibid.*, 1901, *79*, 1025.

5. Avogadro and Dalton : The Standing in Chemistry of their Hypotheses. A monograph, by A. N. Meldrum (1904).

6. A β-Lactonic acid from Acetone and Malonic Acid, by A. N. Meldrum, *J. C. S.*, 1908, *93*, 598. JCS Proc 1908 p. 31

7. The Molecular Complexity of Amides in various Solvents, Part I, by A. N. Meldrum and W. E. S. Turner, *ibid.*, 1908, *93*, 876.

8. The Cis- and Trans-Modifications of 1-Methylcyclohexan 2-ol-4-Carboxylic Acid and their conversion into 1-Methyl $\triangle'$-cyclohexene-4-Carboxylic Acid, by A. N. Meldrum and W. H. Perkin (Jun.), *ibid.*, 1908, *93*, 1416. Proc. Chem. Soc. 1908 167

9. Complex Nitrites containing Potassium and lead. A preliminary note, by A. N. Meldrum, *J. C. S. P.*, 1908, 97.

10. The Composition and Formula of Well's Potassium lead periodide, by A. N. Meldrum, *ibid.*, 1908, 97.

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19. The Rival Claims of William Higgins and John Dalton, by A. N. Meldrum, *ibid.*, 1911, *55*, No. 22.

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27. The Action of Bromine on *p*-Hydroxy and *p*-Methoxy-Sulphonic Acids, by A. N. Meldrum and M. S. Shah, *J. C. S.* 1923, *123*, 1982.

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M. S. SHAH.

Reviews

Elementary Chemical Theory and Problems. By N. M. SHAH, M.Sc., The Karnatak Printing Works, Dharwar. Price Re. 1.

The author has successfully presented in this book a variety of problems bearing on all the topics that an inter. science student is expected to know. The book is divided into 13 chapters. Each chapter begins with a clear and concise explanation of the subject matter of the chapter. Then follow some examples fully worked out and finally a good number of problems for solution. The examples are well chosen some of them having been extracted from question papers set at the University examinations. There is also a chapter on organic analysis which illustrates the methods used in the estimation of the various elements occurring in the organic compounds and the way the empirical and molecular formulæ are calculated. An appendix at the end giving some useful data such as vapour pressure of water at different temperatures, etc., serves a useful purpose.

K. S. N.

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†Only No. 5.

*Only Nos. 2 & 4 (for the purpose of abstracts).

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‡Librarian and Editor, The Academy of Natural Sciences of Philadelphia, Nineteenth and the Parkway, Philadelphia, U. S. A.

Librarian, Division of Plant Industry, 590, Vermeulen Street, Pretoria, Transvaal.

Librarian, the Rice Institute, Houston, Texas, U. S. A.

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CONTENTS

ARTICLES

A CONTRIBUTION TO THE PHYSIOLOGY OF THE RICE PLANT, (COLUMBA VARIETY NO. 42) FROM THE BOMBAY UNIVERSITY .. B. L. DESAI 1

ON THE NUMBER OF CHROMOSOMES OF SOME INDIAN ARACEAE I.—CHROMOSOMES OF ARISAEMA MURRAYI, (GRAHAM) HOOK .. J. J. ASANA & R. N. SUTARIA 24

NOTES ON THE WASPS OF SOUTHERN AND WESTERN INDIA—I. C. J. GEORGE 32

DIMORPHISM AND COAPTATIONS OF THE WINGS OF SPHAERODEMA RUSTICUM FABR. .. .. M. J. PRESSWALLA & C. J. GEORGE 36

THE DEVELOPMENT OF THE FEMALE EFFERENT GENITAL DUCTS IN APIS INDICA C. J. GEORGE & JOHN A. MULIYIL 46

OBSERVATIONS ON GLOMERELLA CINGULATA (STONEMAN) S. & V. SCH. S. L. AJREKAR & J. D. OZA 56

A STUDY OF CERCOSPORA TINOSPORAE SYD. AND ITS ASSOCIATED PYCNIDIAL AND PERITHECIAL STAGES .. .. .. S. L. AJREKAR & J. D. OZA 65

CLINICAL OBSERVATIONS AND LABORATORY FINDINGS IN CASES OF ABDOMINAL TUBERCULOSIS, PARTICULARLY INTESTINAL TUBERCULOSIS, WITH SPECIAL REFERENCE TO CALCIUM CONTENTS OF THE BLOOD IN SUCH CASES .. B. G. VAD 79

SOME COMMON HYDROMEDUSAE OF THE BOMBAY HARBOUR .. S. H. LELE & (Miss) P. B. GAE 90

THE ANATOMY OF DENDROSTOMA SIGNIFER SELENKA ET DE MAN .. P. R. AWATI & L. B. PRADHAN 102

EXPERIMENTS IN ELECTRO-GARDENING .. .. S. S. NEHRU 114

THE MICROBIAL ASPECT OF THE PROBLEM OF MANGO PRESERVATION .. G. PALACIOS & A. K. KARKARE 130

A SHORT NOTE ON THE DISTRIBUTION OF DIFFERENT TYPES OF LINGULA SPECIES ALONG THE WEST COAST OF THE PRESIDENCY OF BOMBAY .. P. R. AWATI & G. R. KSHIRSAGAR 142

OBITUARY

REV FATHER ETHELBERT BLATTER, S. J. 144

LIST OF THESES IN BIOLOGICAL SCIENCES ACCEPTED FOR M. Sc. & M.D. DEGREES DURING 1934-35 147

REVIEWS 149

ACKNOWLEDGMENTS 152

EXCHANGES 156

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// Journal

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VOL. III MARCH 1935 PART V

A CONTRIBUTION TO THE PHYSIOLOGY OF THE RICE PLANT, (COLUMBA VARIETY NO. 42) FROM THE BOMBAY UNIVERSITY

BY

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Rice is one of the most important crops of India. It is prized as an article of food by all classes of people. It is, therefore, natural that the Rice plant should be the subject of scientific study in the different provinces of India, so that by its scientific cultivation yield of rice per acre may be increased. In Bombay Presidency, important results in the cultivation and treatment of Rice plant have been obtained at the Rice Research Station at Karjat (9, 16).

Even though the Rice plant is intensively studied from the agronomical point of view, very few attempts have been made to study its life processes. A study of its life processes is essential to understand the responses made by the plants to the different treatments applied to them ; otherwise the knowledge gained remains more or less empirical in character. In order to understand its behaviour, it is first necessary to know its internal machinery.

With that object in view the study of the physiology of the Rice plant was undertaken in 1926 by Professor R. H. Dastur in collaboration with his post-graduate students at the Royal Institute of Science, Bombay.

"It is intended", he wrote in one of his joint papers, "to make a detailed study of the Rice plant, including the different phases of nutrition, growth, reproduction, which is likely to extend over a period of seven years". It is a happy coincidence that this review is written in the seventh year from that date during which period Professor Dastur's laboratory has made several important contributions both in physiology and in technique. It is here intended to review briefly the work done and the results obtained for those readers who may not be able to read them in the journals in which they are published.

A living cell is an important physiological entity. It is the laboratory of the plant, its storehouse and its despatch office. It is, therefore, natural that in order to understand the life processes of a plant its cell should be studied first. The knowledge derived from the behaviour of the individual cells, could then be extended and utilised in the study of other larger units. Perhaps, with this idea in view Dastur and Baptista (2) studied the osmotic and suction pressures of the Rice plant as one and basic aspect of Rice physiology. Vegetable cell is enclosed in an elastic membrane, the cell wall, which is subject to pressures of two kinds. There is the turgor pressure exerted by the cell sap in the vacuole on the cell wall and there is a counter pressure exerted by the cell wall against the cell contents known as wall pressure. The amount of water that passes into a cell depends upon the difference between the osmotic pressure of the external medium and the osmotic pressure of the cell contents minus the inwardly directed wall pressure. Therefore, the suction pressure of a cell is the difference between the osmotic value of the cell sap and the wall pressure when the surrounding medium is water. The measurement of this suction pressure gives us a true indication of the force with which water passes inside.

Using the plasmolytic method of De Vries, osmotic pressures at different points on the plant surface were determined to obtain an idea of the osmotic pressure existing in different organs and in different parts thereof. Osmotic pressures of the tissues from the leaf base, leaf apex, leaf sheath, root base and root apex were deter-

mined and the average osmotic pressure of the cells from each part worked out. The osmotic pressure in each part showed a periodicity.

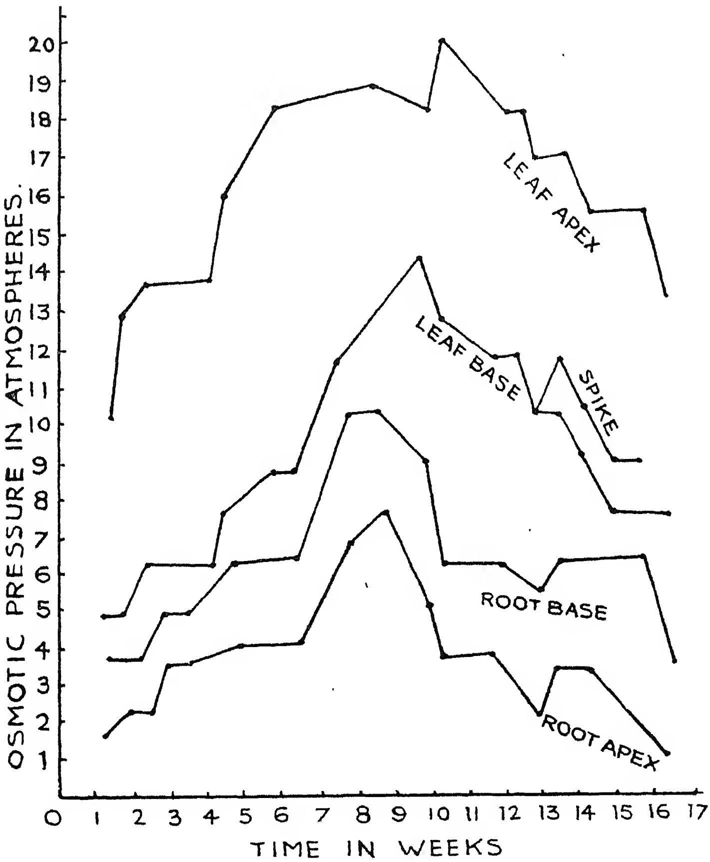

FIG. 1.

Osmotic pressure in different organs of the Rice plant (Columba 42) at different stages.

It is seen from the above figure that in general terms the osmotic pressure of the plant begins to rise as the season advances, reaches a maximum point and then begins to fall ; slight fluctuations are however noticed during the early transplantation stage. A dose of ammonium sulphate increases the osmotic pressure of the roots and the leaves; but the osmotic pressures in these two organs show opposite behaviour. In the roots the osmotic pressure increases from the apex towards the base while in the leaves it increases from the base towards the apex ; but the same relations between the osmotic pressures of root apex and root base and between those of leaf sheath and leaf

apex are maintained during the whole active period. The osmotic pressure in the root varies from 5 to 14 atmospheres and in the leaf from 10·25 to 24·12 atms.

The suction pressure of the same organs was determined during the whole season and it also showed a similar periodicity. Manuring had little effect on the suction pressure. There was a rise of suction pressure at the end of the season and this was an important observation in this investigation. Measurements of osmotic and suction pressures at the end of the season showed that they were nearly equal at that stage.

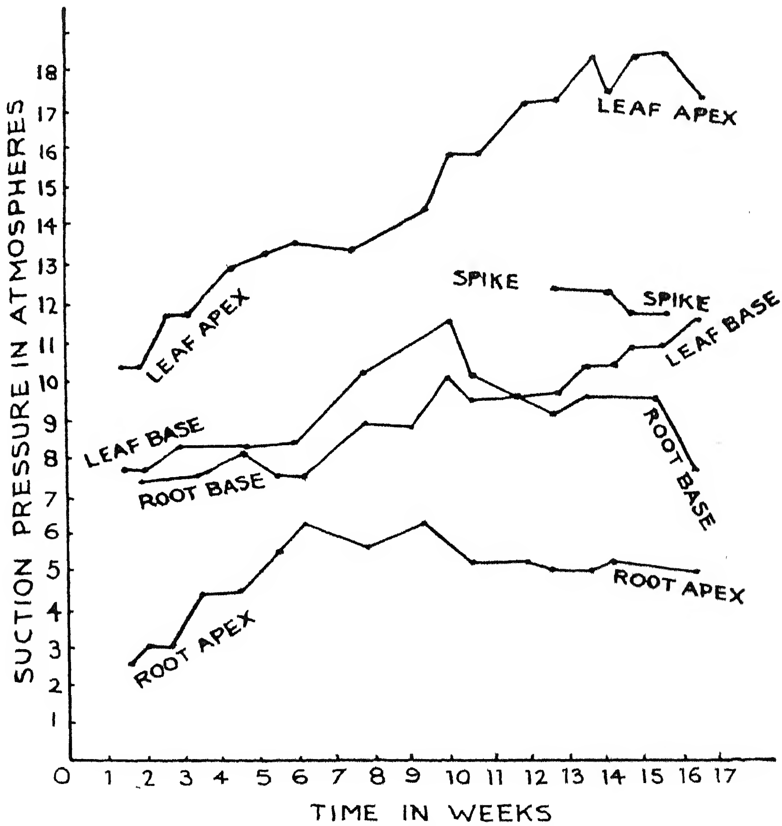

FIG. 2.

Suction pressures in organs of the Rice plant (Columba 42) at different stages.

The suction pressure of the spike showed a continuous rise after which it remained constant. The suction pressure of the root ranged between 2·5 and 6·5 atmospheres at the apex and 7·4 and 10·2 atms. at the base. In the case of leaves it fluctuated between 7·5 and 12

atms. at the base and between 10·5 and 19·3 atms. at the apex.

The effect of ammonium sulphate on the osmotic pressure of the Rice plant clearly points to the conclusion that the osmotic concentration of the cell sap is increased after manuring. In all probabilities ammonium sulphate may be permeable to the roots of the Rice plant and on that may depend its utility as a manure. If the permeability

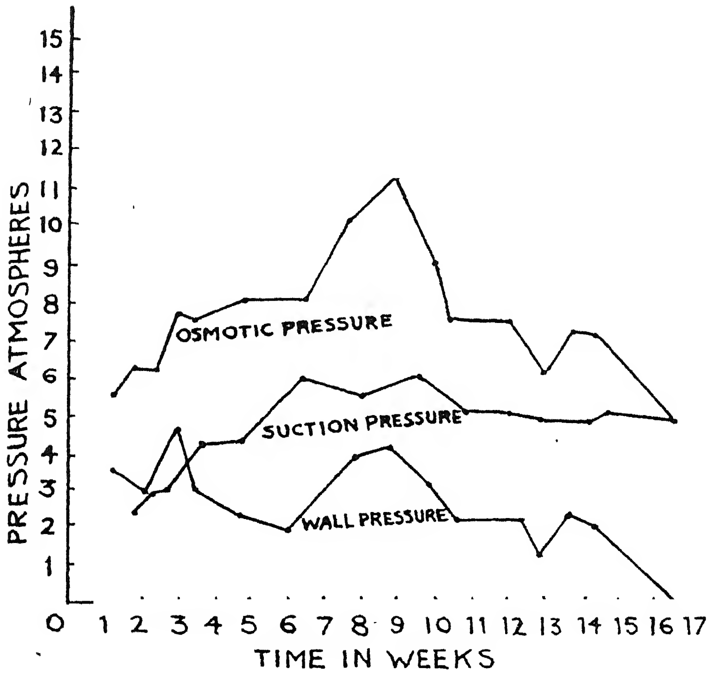

FIG. 3.

Osmotic, suction and wall pressures of root apex of the Rice plant (Columba 42) at different stages.

of a salt can be indicated by a rise of osmotic and suction pressures it would serve as a reliable guide in determining the need of a plant.

Several investigators have worked out the effects of different salts on the growth and yield of Rice plant. Kellner (10), Nagaoka (13), Kelly and Thomson (11), Gile and Carrero (8), Espino (7), are amongst those who have carried out carefully devised experiments on these lines and a mass of information is now available regarding the effect of salts on the growth of the Rice plant. But the effects of different salts on the osmotic pressure of the Rice plant with culture solutions have not been studied and as can be seen above it is capable of giving a very valuable information. It was, therefore, undertaken to pursue further the investigation on the above mentioned lines,

Seedlings grown in the saw dust were transferred to culture jars on the eighth day and the osmotic pressures were determined by the plasmolytic method of De Vries and the plasmometric method of Hoffer. The effect produced by ammonium sulphate solutions of concentration varying from N/100 to N/900 on the osmotic and suction pressure changes was studied. The effect of potassium nitrate solutions of concentration varying from N/100 to N/1500 in respect of these changes was similarly investigated. As a result of these determinations it was found that the osmotic and suction pressures of the roots and the leaves of the Rice seedlings in ammonium sulphate solutions were generally higher than those of the same in corresponding potassium nitrate solutions. There was a big rise in both the pressures after the transfer of the seedlings to ammonium sulphate solutions varying from N/100 to N/500, while no such rise was observed in the corresponding potassium nitrate solutions. Thus, there is a distinct relationship between the absorption of an ion and the respective osmotic and suction pressure set up by it. The chemical analysis shows that NH_4 and SO_4'' ions are considerably absorbed and there is a corresponding rise in the two pressures, while in the case of KNO_3 solutions NO_3 and ions absorbed in minute quantities from solutions of different concentrations and hence there are probably no wide differences in the suction pressures.

The osmotic and suction pressures of the roots and the leaves of the Rice plants when treated with ammonium sulphate and potassium nitrate in the later stages of growth were determined and similar results were obtained. Experiments were also performed with the roots and the leaves of Tradescantia zebrina, Hort. and Zea mays, L. with similar results. There was an increase of osmotic and suction pressures when the salt was supplied and a depression when the same was withheld.

The evidence supplied by Dastur and Cooper (3) shows that the osmotic and suction pressure measurements should serve as a guide for determining the efficiency of a fertiliser and obtaining the knowledge of the ionic requirements of plants. The absorption of ions by plants is a very complicated phenomenon and several workers have approached the subject from different avenues. The unequal absorption of positive and negative ions shown by Meurer (12) has not made the problem less complicated. Pantanelli (14) and Pantanelli and Sella (15) have extended their observations to various other species of plants and confirmed the above observations of Meurer (12). This unequal absorption of the ions of a salt has a far-reaching effect upon the

medium and on the plants grown in it. The medium may be made either more acidic or basic and both these conditions would be abnormal for the plant. It is, therefore, necessary to extend the observations of Dastur and Cooper (3) and supplement them with direct determinations. In order to produce some direct evidence of the unequal absorption of different ions of a salt as suggested from osmotic and suction pressure changes, Dastur and Malkani (5) studied the absorption of ions by entire plants instead of by several tissues.

The Rice plants used in their investigation by Dastur and Malkani (5) were either grown in culture solutions from the very beginning or taken from the experimental beds at different stages and transferred to the culture solutions. Culture jars were embedded in the beds so as to cut off the light reaching the roots. Experiments were started with seedlings eight days old. They were transferred to the culture solutions, the concentration of different ions in which were known. The intake of different ions was determined from day to day by chemical analysis.

TABLE I.

Daily absorption of NH_4 and SO_4'' ions by Rice seedlings from 0·002N $(NH_4')_2\ SO_4''$ solution for ten days.

Age of seedling in days.	Days in solution	absorbed amt. gms.		% of absorbed amount	
		$NH^{\cdot}_4$	SO''_4	$NH^{\cdot}_4$	SO''_4
8–9	1	0·0018	0 0029	5·0	3·0
10	2	0·0029	0·0040	8·0	4·2
11	3	0·0047	0·0067	13·0	7·0
12	4	0·0058	0·0081	16·0	8·4
13	5	0·0072	0·0106	20·0	11·0
14	6	0·0083	0·119	23 0	12·4
15	7	0·0097	0·0139	27·0	14·5
16	8	0·0112	0·0154	31·0	16·0
17	9	0·0117	0·0159	32·5	11·5
18	10	00·118	0·0159	32·5	16·5

The results given in table I clearly show that the two ions are absorbed in unequal amounts for all the ten days. It was also noticed that the absorption of water stops when the absorption of ions ceases.

The results of a second series of experiments to study the intake of NH_4 and SO_4'' from eight different solutions of strengths varying from 0·005 N to 0·0011N during a period of eight days are given below in table II.

TABLE II

The absorption of $NH^{\cdot}_4$ and SO_4'' ions from $(NH_4)_2$ SO_4 solutions of different concentrations by Rice seedlings.

Strength of $(NH_4)_2$ SO_4	Absorption in gms. of		Ratio of absorption of SO''_4:$NH^{\cdot}_4$
	SO''_4	$NH^{\cdot}_4$	
N/200	0·0503	0·0190	2·60:1
N/300	0·0446	0·0180	2·40:1
N/400	0·0244	0·0138	1·70:1
N/500	0·0160	0·0116	1·30:1
N/600	0·0115	0·0098	1·10:1
N/700	0·0092	0·0088	1·00:1
N/800	0·0055	0·0085	0·64:1
N/900	0·0045	0·0084	0·53:1

The striking features evident from the above results are : (1) That the absorption of NH_4 and SO_4'' ions by seedlings decreases as the concentration of ammonium sulphate solution decreases, but if the results are calculated as percentage of total quantities of NH_4 and SO_4'' ions present, then the percentage absorption of SO_4'' decreases and that of NH_4 increases with the decrease of concentration. The direct determinations clearly bear out the fact that the two ions of ammonium sulphate are unequally absorbed and not in the proportion in which they exist in the salt. And (2) that the Rice plants absorb greater quantities of ammonium ions than sulphate ions from solutions of ammonium sulphate at all stages of growth and that the rate of their absorption is independent of the presence or absence of nitrate ions or any other foreign ion. As a result of the greater

absorption of the basic ion than of the acid ion, the solution turns gradually more and more acidic. This fact was confirmed by pH value determinations of the solutions.

The figures 4, 5 and 6 show the absorption of NH_4 SO_4'' and NO_3' ions from different solutions at various stages of growth. It is evident

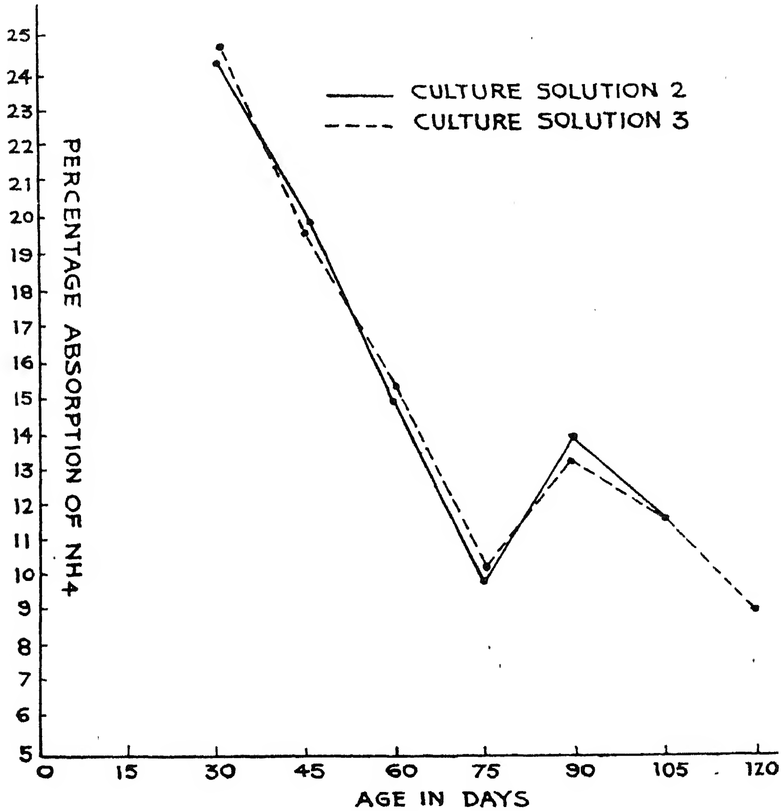

FIG. 4.

Absorption of ammonium ion by the Rice plant (Columba 42) at different stages from two different cultures.

from these figures that the constitution of the culture solution does not affect the absorption of different ions at any stage of growth, their absorption from different culture solutions remaining the same at a particular stage. It is also seen from these three figures that the absorption of ammonium and sulphate ions decreases as the plant grows, while the absorption of nitrate ion increases in the same order. One significant feature borne out by these figures is that the

maximum absorption of nitrate ions by Rice plant is at the flowering stage and then there is a big fall in its absorption.

Since ammoniacal nitrogen is a better source of nitrogen to Rice plant, it was also undertaken to find out the absorption of NH_3 from different ammonium salts. Culture solutions of different strengths were prepared and the plants at different stages of growth were kept in them and the absorbed ion was then chemically determined. From a large number of such determinations it was found that in the earlier

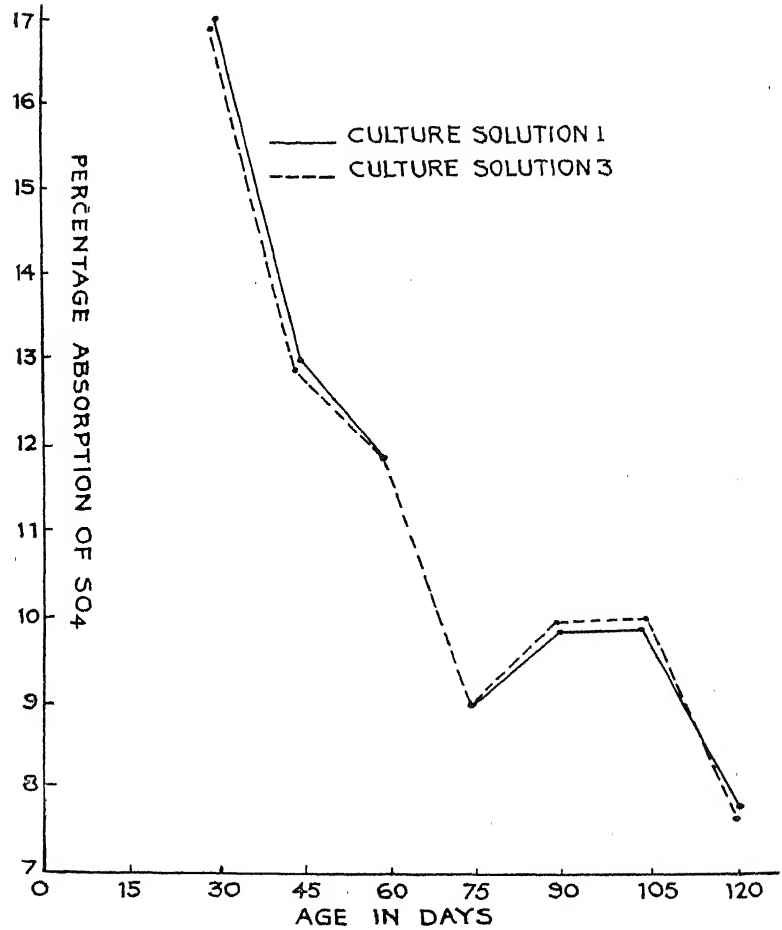

FIG. 5.

Absorption of sulphate ion by the Rice plant (Columba 42) at different stages from two different cultures.

stages of growth the salts stood in the order of sulphate, phosphate, nitrate and chloride of ammonium and in the later stages of growth

in the order of sulphate, nitrate, phosphate and chloride of the same as far as their absorption of ammonium ion was concerned.

We have seen that the absorption of the nitrate ion increases as the plant ages, but its non-absorption from the solution of a nitrate is not caused by the non-absorption of positive ion. Experiments

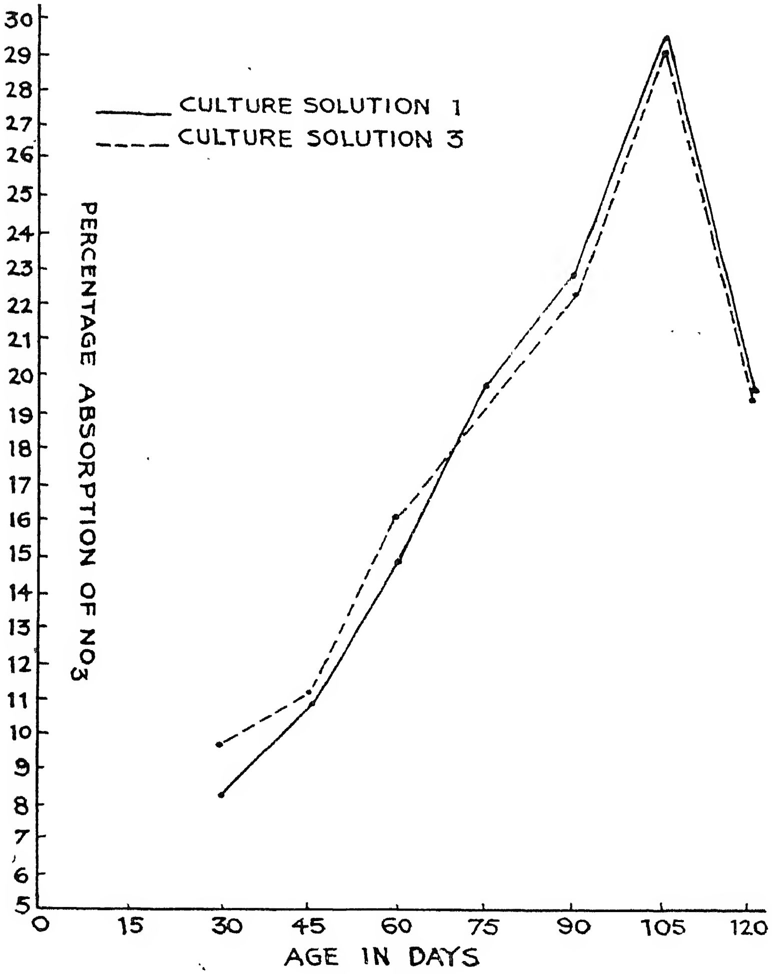

FIG. 6.

Absorption of nitrate ion by Rice plant (Columba 42) at different stages from two different cultures.

were also carried out on plants of different ages using potassium nitrate of various strengths. The results thus obtained show that the absorption of nitrate ion is also independent of the presence or absence of foreign ions. The experiments were also performed to study

the absorption of nitrate ions from different salts. The absorption of NO_3' ions from the solutions of different concentrations of nitrates stands in the order of nitrates of ammonium, magnesium, calcium, potassium and sodium in the earlier stages of growth and in the order of those of ammonium, potassium, magnesium, calcium and sodium in the later stages of growth. Figure 7 shows the amount of NO_3'

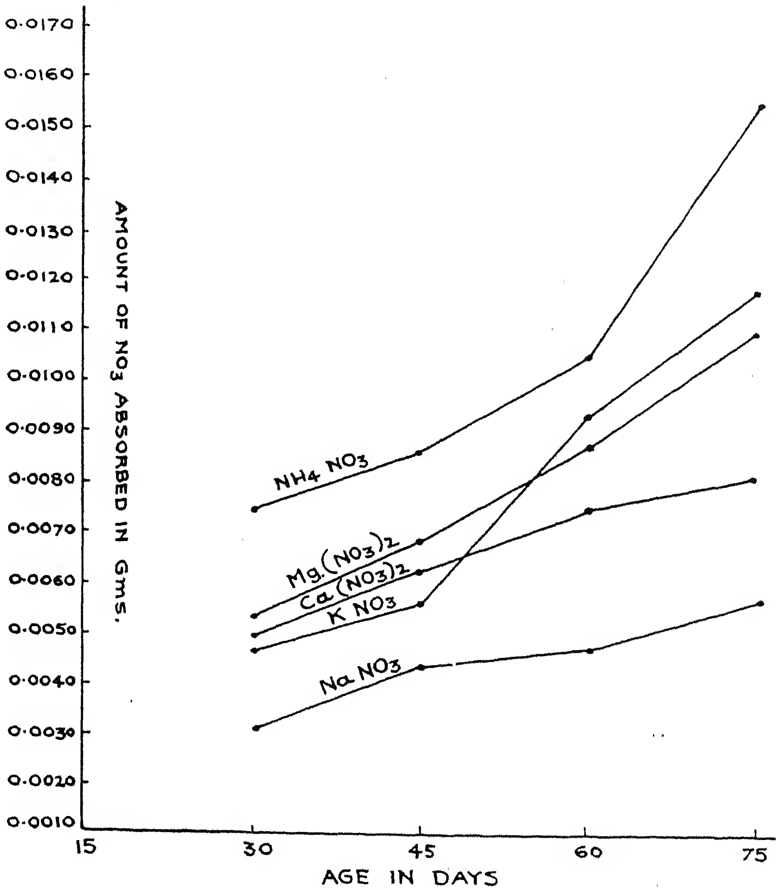

FIG. 7.

Absorption of nitrate ion by the Rice plant (Columba 42) at different stages from cultures containing different nitrates.

absorbed from the different nitrates by the Rice plant at different stages of growth. These results prove that the absorption of nitrate ion is increased as the plant ages, probably on account of the increased permeability of protoplasm to nitrates as it advances in age. The protoplasm is more permeable to NH_3 ion in earlier stages than in

later stages. It is evident from the results so far considered that the absorption of nitrogen by the Rice plant chiefly depends upon the form in which it is given and the stage at which the particular form is supplied.

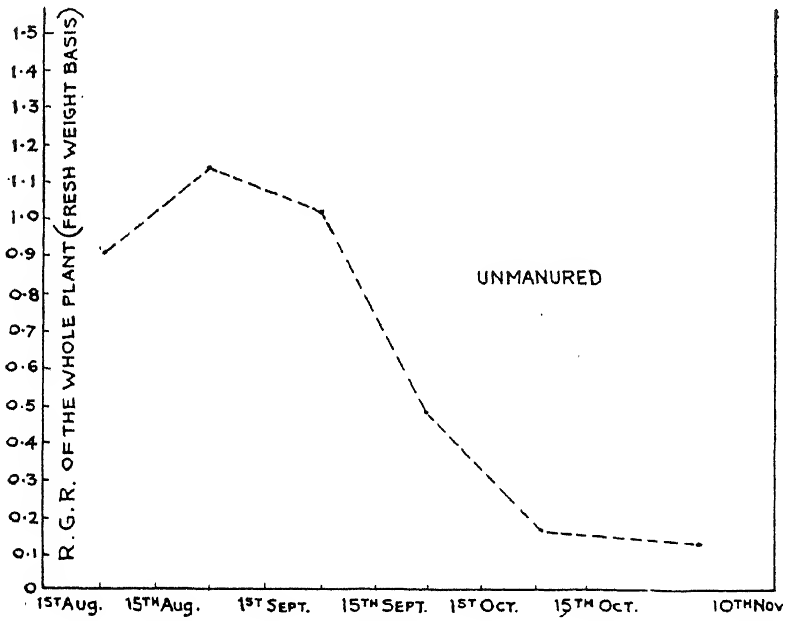

FIG. 8.

Relative Growth Rate of unmanured Rice plant during the season.

If the behaviour of the Rice plant regarding the selective absorption of the different forms of nitrogen at various stages is as it is outlined above, one is tempted to suggest that one form may be given at the early stage and the other form may be given at the late stage. This view, open to objection as it is, is based on the conception that the assimilatory activity of the Rice plant is very great at the flowering stage and hence the nitrates given at that stage should result in the higher yields of straw and grain. But the very important fact that a long period must intervene to allow the nitrates to be incorporated into the substance of the plant is lost sight of. In order to ensure the maximum effect, Dastur and Malkani (5) suggested that the Rice plant be given a mixture of the two forms of nitrogen in a single application. The accuracy of this point was tested by Dastur and Pirzada (6) in their investigation of the growth rate, carbohydrate contents and the yield of Rice plant under different treatments.

Several batches of plants were manured once at an interval of

fifteen days. Sulphate of ammonia, potassium nitrate and a mixture of these two on equal nitrogen basis were the three treatments separately given to one of these batches, only one application of any one of the three treatments was given to a batch. One batch was entirely kept unmanured. Determinations of fresh and dry weights of leaves, culms and roots, volume of roots and leaf area were made separately every fortnight for all the manured and the unmanured plants and the relative growth rate was worked out according to the formula :

$$R.\ G.\ R. = \log e\ W_1 - \log e\ W_0$$

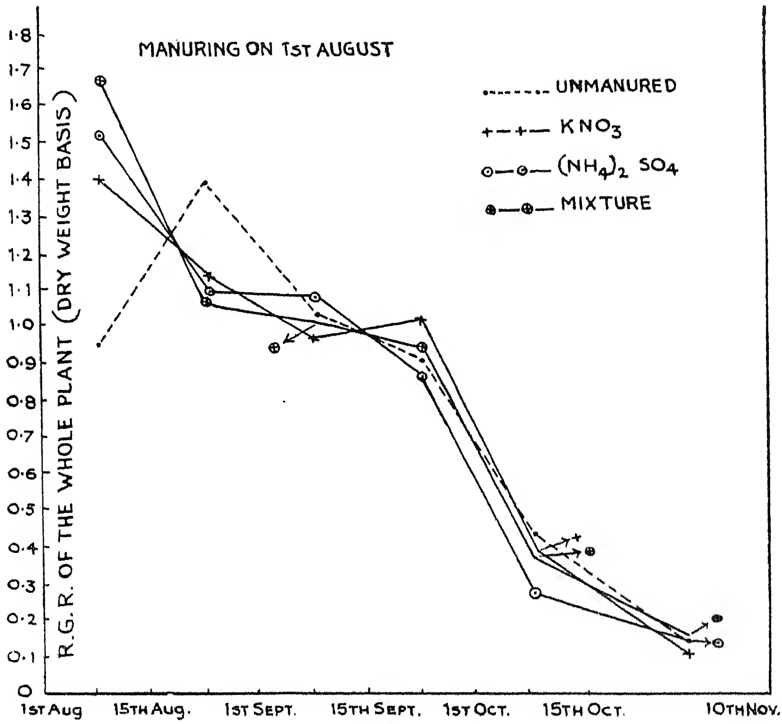

FIG. 9.

Relative Growth Rate of the Rice plants (Columba 42) at different stages when manured with potassium nitrate, ammonium sulphate and a mixture of the above two on equal nitrogen basis respectively on 1st August as compared with that of the unmanured.

when W_0 and W_1 are the dry weights of the whole plant on two consecutive periods. Similarly the R. G. R. of the leaf from the leaf area was also worked out. The carbohydrate analyses were made according to the improved method of Dastur and Samant (6A). Weights of straw and grains yielded under different treatments were also noted.

Figure 8 shows that the relative growth rate in the case of unmanured plants reaches its maximum in the period between 15th August and 1st September. It is highly interesting to compare the graph in figure 8 with those in figures 9, 10, 11, 12 and 13. In the case of the plants manured on 1st August the control series shows the highest growth rate in the second half of August while in those manured on 15th August the mixture series shows the highest growth rate for the

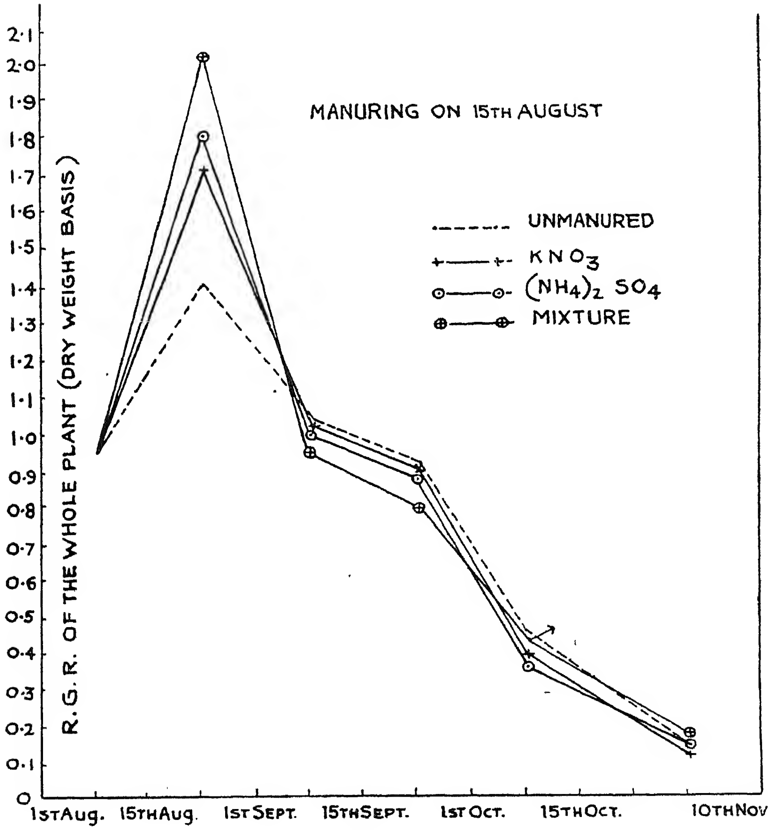

FIG. 10.

Relative Growth Rate of the Rice plants (Columba 42) at different stages when manured with potassium nitrate, ammonium sulphate and a mixture of these two on equal nitrogen basis respectively on 15th August as compared with that of the unmanured.

same period. Of all the subsequently manured series of plants, the mixture treatment fares the best and although the growth rate is kicked up in the fortnightly period that follows, there is a very great fall immediately afterwards. It is also evident that the late manuring has little effect on the growth rate.

The carbohydrate contents of the Rice plants determined on the corresponding dates and under the same treatments show great similarity of features as the relative growth rate. Maximum carbohydrate contents are met with in plants manured on 15th August. The growth rate curves under different treatments and the results of the carbohydrate contents clearly suggest the usefulness of early manuring. These experiments were repeated in the next year and they yielded similar results. The same features of growth and carbohydrate contents were found in plants manured on the 15th August. The best form in which nitrogen should be given is the mixture of ammoniacal and nitrate nitrogen as is also borne out by these results.

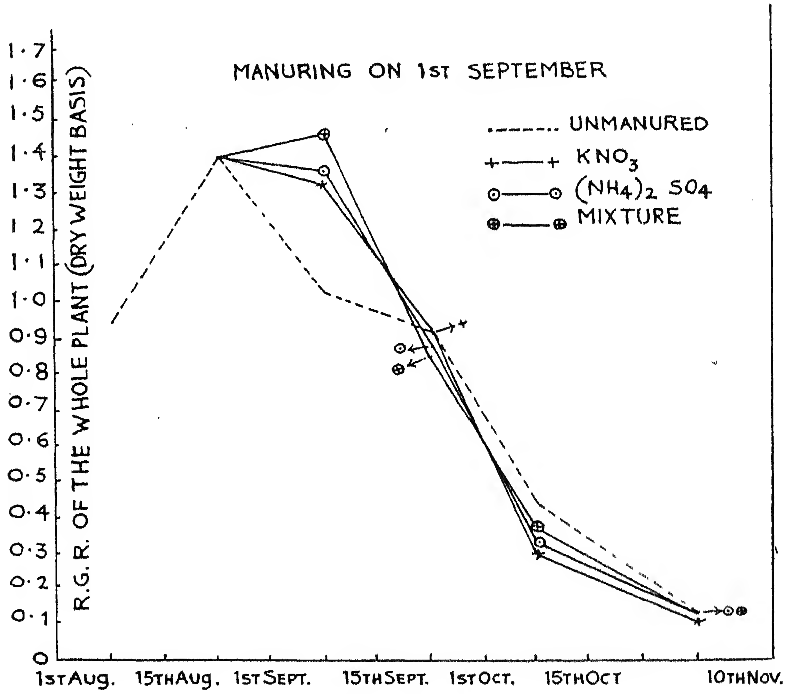

FIG. 11.

Relative Growth Rate of the Rice plant (Columba 42) at different stages when manured with potassium nitrate, ammonium sulphate and a mixture of these two on equal nitrogen basis respectively on 1st September as compared with that of the unmanured.

In order to determine whether the maximum beneficial effect of early manuring was specific for nitrogenous fertilisers only or it was the same with other fertilisers, a set of experiments were planned out with superphosphates as the manure similarly applied. Growth rate and carbohydrate contents of the plants manured with superphosphates showed the beneficial effect of the early manuring. Super-

phosphates are generally known to increase vegetative growth to a greater extent than reproductive growth. The findings of Dastur and Pirzada (6) regarding the superiority of the mixture treatment and of the early manuring of Rice plants have been tested in the fields at various places in the Bombay Presidency for the last three years and the results of these tests along with the nitrogen contents of the Rice plants under these treatments will be subsequently published.

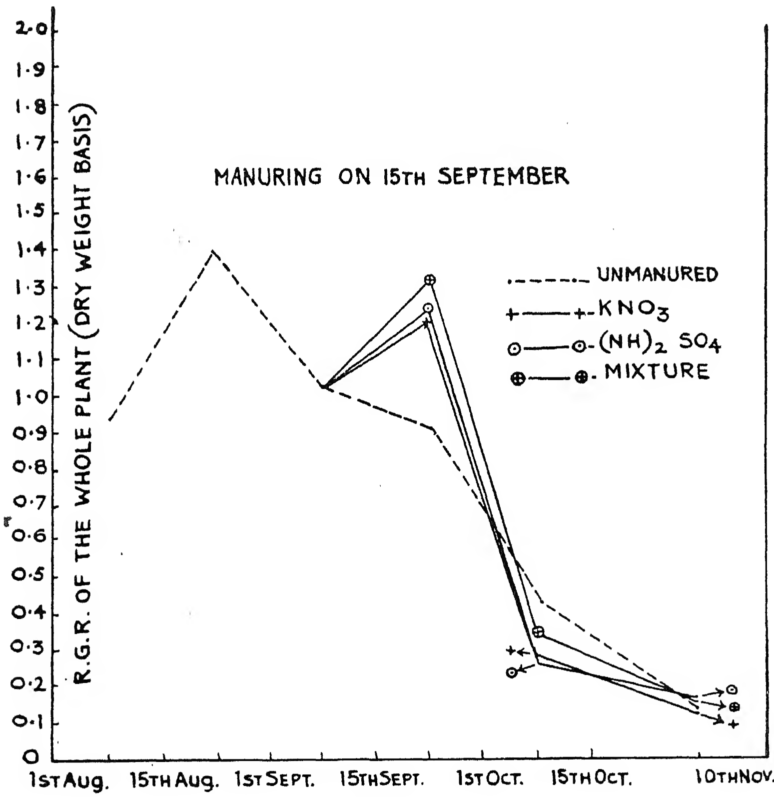

FIG. 12.

Relative Growth Rate of the Rice plant (Columba 42) at different stages when manured with potassium nitrate, ammonium sulphate and a mixture of these two on equal nitrogen basis respectively on 15th September as compared with that of the unmanured.

Dastur and Malkani (5) showed that the absorption of ammonium ion decreases and that of nitrate ion increases as the plant advances in age. They suggested that the difference in permeability of the protoplasm at different stages of growth may be responsible for this behaviour. If it is admitted that this behaviour is the net result of the reaction between the plants and their external media,

the investigation of the intake of nutrients is not complete without an investigation of the hydrogen ion changes in the plant and its medium. So an investigation of the hydrogen ion changes when Rice plants are treated with different nitrogenous fertilisers was undertaken by Dastur and Kalyani (4). Their investigation was divided into three parts. Firstly they studied the pH changes of the soils and of the roots and

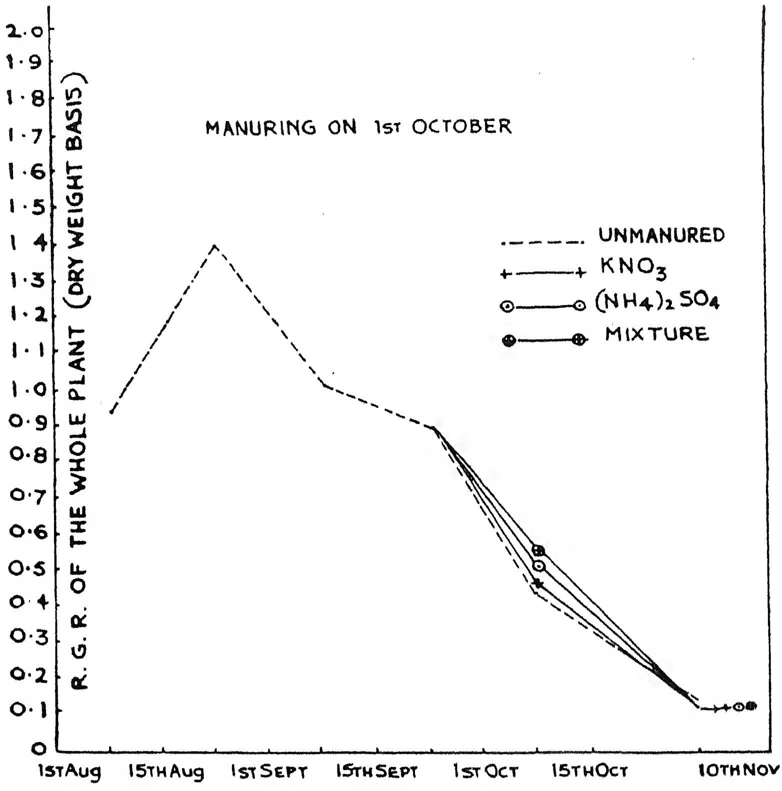

FIG. 13.

Relative Growth Rate of the Rice plant (Columba 42) at different stages when manured with potassium nitrate, ammonium sulphate and a mixture of these two on equal nitrogen basis respectively on 1st October as compared with that of the unmanured.

leaves of the Rice plants at different stages of growth when differently treated. Secondly they determined the pH values of the culture solutions and of the roots and leaves before and after the plants were kept in them and thirdly they determined the iso-electric points of the principal proteins of roots and leaves of the Rice plants. Electrometric method was used to measure the hydrogen ion concentration.

The pH values of the soil from beds under different treatments

are given in figure 14. It is seen that the soil from the unmanured bed becomes alternately acidic and alkaline twice during the whole season, while that manured with sodium nitrate shows a persistent alkaline tendency throughout the major part of the season.

The soil manured with ammonium sulphate undergoes alternate changes similar to those of the unmanured soil. The pH values of the soil manured with a mixture of ammonium sulphate and sodium nitrate on equal nitrogen basis do not drop down as low as those of the soil manured with ammonium sulphate and from the end of October show a behaviour similar to the unmanured ones. The highest acidity of the soil manured with ammonium sulphate seems to be a very natural consequence of the greater intake of ammonium ion than that of

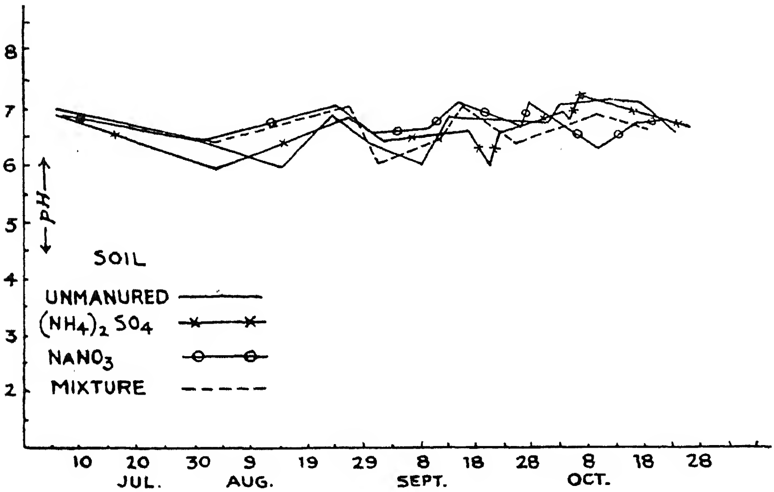

FIG. 14.

Hydrogen ion concentration of the unmanured soil from the Rice beds and those manured with ammonium sulphate, sodium Nitrate and a mixture of these two on equal nitrogen basis respectively at different stages.

the sulphate ion in the early stages by the Rice plant. The reactions in the culture solutions are exactly of the same nature.

The pH values of the roots of the plants manured differently show a very great general similarity under all treatments. Although they differ in magnitude, the curves show almost identical character. Generally speaking the pH values are the lowest in all cases during August and the first week of September; after this there is a rise which is kept up for the remaining period. This rise in the pH values is greater in roots from manured beds than in those from unmanured beds. Roots from the bed under mixture treatment are

less acidic than those from the beds manured with ammonium sulphate in the early stage ; reverse is the case after the last week of October till the end of the season.

In the last week of October the pH value of the roots is 4·6. This is probably the period when the proteins reach their iso-electric point and the protoplasm undergoes heterosis due to aging. This point is confirmed by the fact that the pH value of the inflorescence is the same as the pH value of the leaves.

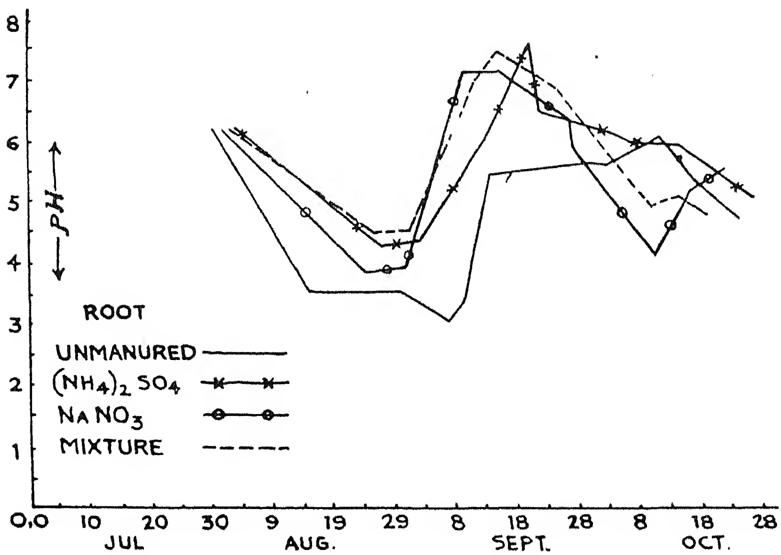

FIG. 15.

Hydrogen ion concentration of the roots of the unmanured Rice plants and that of the roots of the plants manured with ammonium sulphate, sodium nitrate and a mixture of these two on equal nitrogen basis respectively at different stages of growth.

Figure 16 shows the pH values of the leaves of the Rice plants treated as above. The changes in the pH values fluctuate between pH 5·9 and 6·2 . In ammonium sulphate treatment, the changes in pH values are comparatively great and frequent. As expected the ammonium sulphate treatment results in more acidity than the rest. The pH values of leaves begin to rise in August, attain the first maximum towards the end of August, reach their minimum in the middle of September and reach the second maximum point in the second week of October, after which there is a fall. The points of maxima in the case of leaves coincide with the points of minima of the roots. The iso-electric points of the plant tissue lie between pH 4·1 and 4·4.

This investigation has shown why the ammonium ions are more

taken up in the early stage and nitrate ions are taken up in the later stage by the Rice plants. The permeability of gels, as shown by Bigwood (1), is chiefly controlled by diffusion and by chemical reaction between the penetrating ions and the electrolytes present in the gel. The pH values of the roots lie on the alkaline side of the iso-electric point in the first month and hence the basic or ammonium ion is selectively absorbed. It reacts with the electrolytes and pro-

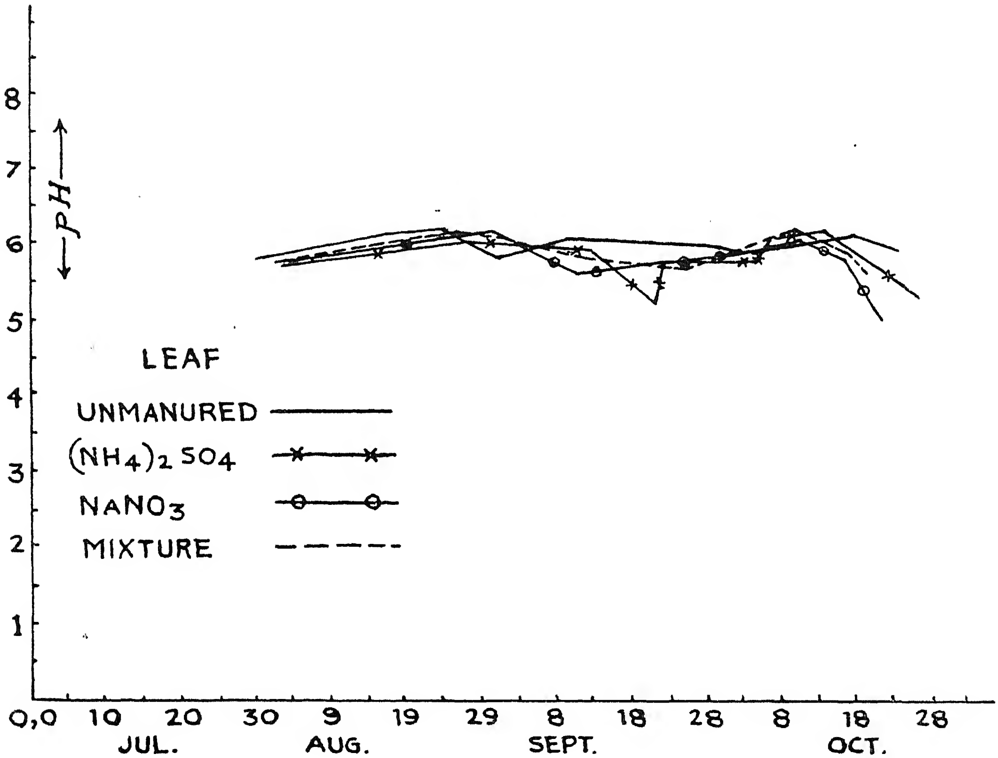

FIG. 16.

Hydrogen ion concentration of the leaves of the Rice plants (Columba 42) manured with ammonium sulphate, sodium nitrate and a mixture of these two on equal nitrogen basis respectively and that of the leaves of untreated plants at different stages of growth.

duces indiffusible substances. The proteins of the protoplasm dissociate more into COOH groups which bring about acidity. The proteins of the roots are now in acid medium and on the acidic side of the iso-electric point, hence the acidic ions are more taken up than the basic ions. For this reason nitrate ions continue to be absorbed during the later stages. The nitrate ions thus absorbed will have to be neutralised and therefore the dissociation of NH_2 groups of proteins occurs. This brings about the alkalinity of the cell sap

of the roots. This investigation has not only confirmed the results of the previous investigations, but has also explained why the Rice plant behaves in this manner regarding the absorption of anions and cations at different stages from different sources. It has opened out a line of research that can be endlessly and profitably pursued in the case of other crop plants. If the physico-chemical conditions of the cell sap of these plants are studied extensively, it will throw great light on the much debated subject of plant nutrition.

It will be seen from the above account that some very important researches in the physiology of Rice plant have emanated from the Bombay University. The Bombay Department of Agriculture has produced some very useful work from general agricultural point of view and Professor Dastur's laboratory at the Royal Institute of Science has tried to supply useful and accurate basic knowledge in Rice physiology. He started his researches with the study of the osmotic and suction pressure changes in the cells from the tissues of the Rice plant and gradually has so developed his line of research that it is likely to be useful both in agriculture and plant physiology. It will not be out of place to mention that his investigation into the effectiveness of the mixture of ammoniacal and nitrate forms of nitrogenous fertilisers has received a confirmation from Titabar Farm, Assam, where they have obtained similar results. A striking feature of Professor Dastur's researches that will be evident from the foregoing account is that he has developed the subject in a most natural way. He has pursued his researches with a definite plan and purpose and arrived at conclusions of outstanding importance. His work on Rice physiology was recognised in the form of a grant made to him by the Imperial Council of Agricultural Research of India which has enabled him to work out the problem of nitrogen nutrition of the Rice plant. Many interesting problems still remain to be tackled and it is expected that Professor Dastur and the Rice Specialist at Karjat will make a substantial contribution that will enable us to enhance our rice producing capacity.

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ON THE NUMBER OF CHROMOSOMES OF SOME INDIAN ARACEÆ.

I. CHROMOSOMES OF ARISÆMA MURRAYI, (GRAHAM) HOOK.

(*The Cobra or Snake Lily*).

By

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(*Received 21st December, 1934*)

INTRODUCTION

Though Araceæ is a fairly large natural order, according to Blatter and McCann (3) it is represented in the Bombay Presidency only by 13 genera comprising 35 species. The Araceæ have received sufficient attention from the systematists but they have not had their due from the students of cytology. This appears rather strange, considering the fact that this order includes some very curious and interesting plants. It is very probable that the difficulty of procuring and preserving suitable material has had much to do with this. Some research work on the embryology of Aroids has been done by Campbell (4, 5, & 6), Gow (9, 10 & 11), Mitchell (13), and Mottier (14) but so far the study of the microsporogenesis of these peculiar plants has received very little attention.

Regarding the chromosomes of Arisæma so far only two species have been reported upon. Atkinson (2) gives sixteen as the haploid number of chromosomes in Arisæma triphyllum, and in A. serratum var. Thunbergii Yamakawa (Ishikawa 12) has reported verbally the diploid number as twenty-six. Whilst against the observations of these two previous investigators, the senior author Asana (1) has reported that in Arisæma Murrayi, the diploid number as seen in the root-tips is twenty-eight, while the haploid number is fourteen as observed in the division process of the pollen mother-cells.

Table I gives a complete list of the numbers of chromosomes in the Araceæ compiled from all the available literature (8, 12 & 16.)

TABLE I.

Reported Chromosome Numbers in the Araceæ.)

(*ca=about*)

Species	N	2 N	Reported by
Anthurium acaule	15	...	Gaiser 1927
„ acutangulum	ca. 15	...	„ „
„ Andraeanum	ca. 15	...	„ „
„ „	16	...	Haase—Bessell 1928
„ Bakeri	ca. 15	30	Gaiser 1927
„ Beyrichianum	ca. 15	...	„ „
„ Brownii	ca. 15	30	„ „
„ comtum	15	...	„ „
„ cordatum	ca. 15	30	„ „
„ crystallinum	ca. 15	...	„ „
„ denudatum	ca. 15	...	„ „
„ Dominicense	ca. 15	...	„ „
„ gracile	15	...	„ „
„ grandifolium	ca. 15	30	„ „
„ Guildingii	ca. 15	...	„ „
Ahthurium gymnopus	ca. 15	30	„ „
„ hacumense	ca. 15	30	„ „
„ Hookeri	ca. 15	...	„ „
„ litorale	15	...	„ „
„ magnificum	ca. 15	...	„ „
„ „	16	...	Haase—Bessell 1928
„ maximum	ca. 15	...	Gaiser 1927
„ nymphaeifolium	ca. 15	30	„ „
„ Olfersianum	ca. 15	...	„ „
„ pedato-radiatum	ca. 15	...	„ „
„ recusatum	ca. 15	...	„ „
„ Scherzerianum	ca. 15	...	„ „
„ „	16	...	Haase—Bessell 1928

Species	N	2 N	Reported by
Ahthurium subsignatum	ca. 15	30	Gaiser 1927
„ tetragonum	15	...	„ „
„ Tuerckheimuii	ca. 15	...	„ „
„ undatum	ca. 15	30	„ „
„ variabile	15	...	„ „
„ Veitchii	15	...	„ „
„ Warocqueanum	ca. 15	30	„ „
„ scandens	ca. 24	...	„ „
„ radicans	25	50	„ „
„ crassinervium	ca. 30	...	„ „
„ digitatum	ca. 30	60	„ „
„ Wallisii	ca. 30	60	„ „
Hybrids Anthurium Chelseiense	ca. 15	30	„ „
„ „ ferrierense	...	ca. 30	„ „
„ „ Froebelii	ca. 15	30	„ „
„ „ "gloriosum"	ca. 15	...	„ „
Hybrids Anthurium roseum Hort.	...	ca. 30	„ „
Aglaonema versicolor	8	...	Gow 1908
Arisaema seeratum Arisaema Thunbergii	14	26	Yamakawa (Ishikawa) 1916
„ triphyllum	16	...	Atkinson 1899
Arum cornutum	16	32	Haase—Bessell 1930
„ macratum	...	ca. 32	Schmucker 1925
Dieffenbachia daraquiniana	8	16	Gow 1908
Peltandra undulata	ca. 22	...	Dugger 1900
Richardia africana	16	...	Overton 1909
„ „	12	...	Michell 1916
Spathiphyllum Patinii	9	...	Jiissen 1928
Symplocarpus foetidus	8	...	Gow 1907
Xanthosoma sp.	16	...	Gow 1913
Zantedeschia aethiopica	16	...	Overton 1909

Material and Methods

Arisæma Murrayi—the common Cobra or Snake-Lily grows wild at Mahabaleshwar. It begins to appear in large numbers from about the beginning of the fourth week of May. Very young stages of the purely male spadix were fixed from the plants which were almost underground, or whose tops had just begun to appear above the sub-soil.

According to Blatter and McCann (2) the spadix in Arisæma Murrayi may be androgynous or unisexual. They have seen and described in detail both the androgynous and pure male spadix but they have not met with any plants bearing pure female spadix. Gow (11) reports that Arisæma seldom bears staminate and pistillate flowers on the same spadix, but the indication is that the plant that bears pistillate flowers one year bears staminate flowers the next. In view of this very important fact we have kept some plants under observation and a detailed account of their morphology and cytology will be presented in the near future.

For the fixation of the root-tips the tubers were carefully removed from the ground and rinsed in tepid water. The delicate root-tips were cut with a safety razor blade and fixed in a modification of Flemming's fluid. After fixing and washing the material for twenty-four hours, it was very gradually dehydrated and preserved in 70 per cent. alcohol.

The young spadix was cut into small pieces and these were fixed in Navashin's Fluid. This solution consists of :—

Chromic acid 1 p. c. aq. sol.	15. c. c.
Formalin (40 Vols.)	4 c. c.
Acetic acid, glacial	1·5 c. c.

The material was fixed for 24 hours. During this time the fixative was changed only once. The pieces were washed in running water for 24 hours, were very gradually dehydrated and preserved in 70 per cent. alcohol.

Xylol was used as a clearing agent and 52° paraffin for embedding. Sections were cut at the thickness ranging from 9 to 12 microns. The sections of the material fixed in modified Flemming were bleached in a solution of 20 vols. hydrogen peroxide dissolved in 90 per cent. alcohol, in the proportion of 1 to 3, for about 24 hours, and stained with Haidenhain's iron alum hæmatoxylin.

Observations

After the transverse segmentation of the spireme is completed the chromosome pairs lie scattered in the nuclear cavity. At early diakinesis (Fig. 1) the bivalent chromosomes are in various forms. The

homologues may either lie side by side, get twisted round one another, or they join end to end. Occasionally they form a ring or the figure of 8. Rings of more than two chromosomes have also been noticed at this stage. Atkinson (2) in Arisæma triphyllum and Overton (15) in Richardia africana, both these authors describe ring-forms taking place in the plants they have studied. The disappearance of the nucleus takes place quite abruptly at a comparatively early stage in the microsporogenesis of Arisæma Murrayi.

During the late diakinesis the chromosomes, as they condense, grow thicker and get very much shortened. Such slightly condensed, short bivalents stand well apart from one another for a considerably long period in a clear nuclear space bounded by a membrane which is seen quite distinctly even at this stage.

On the disappearance of the nuclear membrane the fibrillae begin to extend into the nuclear cavity from the surrounding cytoplasm and they get quickly organised into a multipolar spindle which is soon changed into a bipolar one. The chromosomes become much more condensed, the members of each bivalent pair coming into very close contact with each other. A few instances were observed in which nuclear membrane seemed to have disappeared just before or as a few spindle fibres came into view (Fig. 2).

There is nothing unusual to record regarding the arrangement of the chromosomes in the equatorial plate and their separation during the metaphase stage which is of a comparatively long duration. It seems that the chromosomes now take up the stain more deeply than at any other stage and therefore the metaphase chromosomes arranged on the equator have the appearance of solid rods. Fig. 3 shows a polar view of an equatorial plate with fourteen chromosomes placed in different planes. As the spadix is cut transversely, looking down upon the chromosomes in a polar view, they seem to be somewhat quadrangular. Whether it is due to Navashin's fluid or not we are not in a position to say but we failed to find any tetrad formation at this stage as described by Atkinson (2) and Duggar (7).

On going through the list of the chromosome numbers in Araceæ, one finds that the number of chromosomes varies in different species of the genus Arisæma. Atkinson (2) records 16 as the haploid number in Arisæma tryphyllum while in A. serratum var. Thunbergii Ishikawa (12) gives 26 as the diploid number reported to him verbally by Yamakawa.

To ascertain the diploid number of chromosomes in the plant under investigation a number of root-tips were sectioned. A very large number of cells were found fixed in a state of active division. Figs. 4 and 5 are the polar views at the metaphase of 28 somatic chromo-

somes as very commonly found in the peripheral region of the root-tip. The somatic chromosomes are either rod-shaped or J. shaped. The split in the somatic chromosomes during metaphase is not observed. Almost all chromosomes look homogeneous and uniformly stained. It is probable that their dual nature is obscured due to the very close approximation of the members of a pair and the deep staining reaction which the chromosomes of this plant exhibit at the metaphase both in mitosis and meosis.

A side view of an early anaphase shows that the homologous chromosomes are equally distributed on both sides of the equatorial plate. Fig. 6 shows the polar view of the chromosomes at the hetero-typic anaphase. The chromosomes are distinctly 14 in number. Some of the anaphase chromosomes appear to be double, which clearly indicates the beginning of the homœotypic separation. In the late anaphase when the chromosomes reach the poles the spindle is very broad but does not show any split in the middle. However, as soon as the daughter nuclei are reorganised the spindle becomes barrel-shaped and shows a distinct broad split in the middle. Fig. 7 shows one of the daughter nuclei with 14 chromosomes. The nuclear membrane is very clear and the irregular constricted chromosomes remain more or less distinct, and they are not deeply stained.

The interphase is gone through very quickly and the prophase of the second division was not observed. Fig. 8 shows the metaphase of the homœotypic division with one spindle showing a tangential view of the chromosomes at the equatorial plate while the 14 chromosomes of the other spindle present a polar view. Many of the chromosomes are now double and they are very deeply stained. Fig. 9 represents a typical polar view of both the metaphase plates. Early anaphase stages of the second or equatorial division are not commonly met with, and the cells are often observed in the late anaphase and telophase. Fig. 10 represents the polar view of both the anaphase groups. The chromosomes are now smaller and mostly angular, and can easily be counted, their number being 14. Occasionally the two spindles of the homœotypic division are found lying at right angles to each other. Fig. 11 represents one whole spindle showing the fused chromosomes forming a condensed mass at the two poles while the other spindle is represented by a group of 14 chromosomes at the late anaphase in a polar view.

SUMMARY

(1) The number of the haploid chromosomes as counted in polar views of the heterotypic and homœotypic metaphase and anaphase is 14.

(2) In the late diakinesis and the metaphase the chromosomes do not form tetrads.

(3) The first or heterotypic division brings about the reduction in the number of the chromosomes.

(4) The number of the diploid chromosomes as counted in the root-tips is clearly 28.

(5) The prophase stages of the second division have not been observed.

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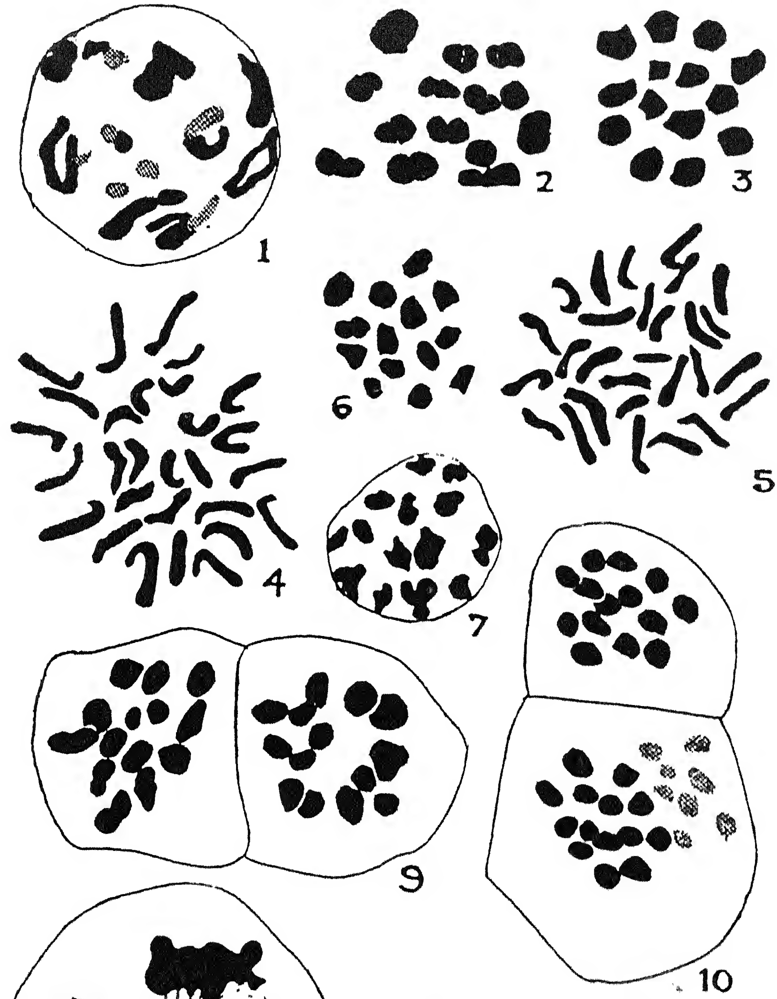
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EXPLANATION OF PLATES

Drawings were made with the aid of the Abbe camera lucida at stage level. All figures were drawn under a 2 mm. immersion Zeiss apochromatic lens (N. A. 1. 40) with Zeiss compensating occular 20X. Figures reproduced without reduction.

Fig. 1. Late diakinesis.

Fig. 2. Bivalent chromosomes without any spindle fibres.

Fig. 3. Polar view of the heterotypic metaphase showing fourteen chromosomes.

Figs. 4 & 5. Polar views of twenty-eight diploid chromosomes from the root-tips.

Fig. 6. Polar view of the heterotypic anaphase showing fourteen angular chromosomes.

Fig. 7. One of the daughter nuclei at the early telophase.

Fig. 8. Homœotypic metaphase.

Fig. 9. Polar view of the homœotypic metaphase with fourteen chromosomes.

Fig. 10. Polar view of the homœotypic anaphase with fourteen chromosomes.

Fig. 11. Late homœotypic anaphase.

NOTES ON THE WASPS OF SOUTHERN & WESTERN INDIA I.

By

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(*With one Plate*)

(*Received 18th January, 1935*)

Entomologists are unanimous in regarding the Hymenoptera as the most advanced group of insects. The intricate social organisation and the high state of development of the nervous system necessary on that account, will entitle the bees, wasps and ants to the highest position not only amongst the insects, but also among the whole group of invertebrate animals. Tropics abound in the number of species of these insects. Their curious mode of life and diverse habits will afford stimulating fields of investigation. Excluding the very showy butterflies and moths, the wasps and ants are the commonest insects which attract our attention. To an observer of nature in its manifold ways of expression the wasps offer an irreconcilable picture of ferocity coupled with tenderness. They are most aggressive to an intruder, most devoted to their young. A hunting wasp seems to surpass even a cat in alertness. The vibrations of its antennae, the ready flutterings of its wings, nay, its whole attitude is one of unflinching pursuit of the game. The still hovering of a Sceliphron centering its vision all round a ceiling in quest of an unwary spider does not fall short of that of a kite directing its look from the horizon, hundreds of feet below over a wandering chick. The rapacious greed for flesh shown by a parasitic wasp is equal to that of a ruthless carnivore. In quaintness of form and brilliance of colour some wasps rival the most brilliant beetles and butterflies. The bees and ants among the Hymenoptera are well-known for their industry. The wasps, though the less known, are nevertheless as industrious as others.

In this paper short notes on some species of wasps which I have had the occasion to collect and observe during the course of the last few years, are given.

1. SPHEX LOBATUS, FABR.

Bingham, Fauna of British India. Hymenoptera, Vol. I.

Lefroy, Jour. B. N. H. S., Vol. XV.

Beadnell, Jour. B. N. H. S., Vol. XVII.

Hingston, Jour. B. N. H. S., Vol. XXX.

This is one of the most beautiful of Indian insects. It has a brilliant metallic blue colour which shows a variation up to a bright green. The variation in size is very common in many of the wasps and S. lobatus varies ordinarily from 20 m.m. to 30 m.m. The variation recorded by Bingham is 22 to 88 m.m. It is commonly found during the hot weather after the first few showers are over. With the first showers, the crickets which these collect to fill the nests with, are also found in large numbers. It is a quick flier and it can carry a cricket three times its own weight with ease. Its hunting habits consist in examining the surface of the ground, gently tapping it with its antennæ and if it was found hollow to dig the earth with its mouth-parts and legs and briskly snatch its victim with its mandible and legs and administer two or three stings according to the size of the animal and then return to the nest.

Locality :—Collected from Travancore, Coimbatore and Bombay.

2. SCELIPHRON SPINOLAE, LEPEL.

Bigham, Fauna of British India. Hymenoptera, Vol. I.

Sharp, Cam. Nat. Hist. 1922.

Horne, Trans. Zool. Soc. Vol. VII.

An account of the habits of an allied species is given by Horne (Cam. Nat. Hist.). I collected this species from a finished nest in Central Travancore. It builds its nest in houses attached to the walls. The nests are about 11 cm. long and 8 cm. in diameter. It covers the nest with a thin coating of a dark green material presumably cow-dung. The species of this genus possess the habit of disguising their nests in different ways. Probably this coating with cow-dung is one of such. The nests are stored with spiders. This is the first time its nest is recorded. A sketch of the nest is given in fig. 1.

Locality :—Collected from Travancore.

3. SCELIPHRON VIOLACEUM, DAHLB.

Bigham, Fauna of British India. Hymenoptera, Vol. I.

Horne, Trans. Zool. Soc. Vol. VII.

This species unlike the other Indian species of the genus has a

cobalt-blue colour. It has a wide distribution. It is a common visitor to human dwellings in search of the small spiders which web the walls and the ceilings. It is the smallest of Sceliphron species.

Locality :—Collected from Bombay.

4. ICARIA MARGINATA, SMITH.

Bigham, Fauna of British India. Hymenoptera, Vol. I.

This is a common social wasp found near human dwellings throughout southern and western India. A sketch of its nest is given in fig. 2. It builds its nest under cover of creepers, on the under surface of leaves of crotons etc. The nest is supported on a short pedicel and consists of paper-like material mixed with wax. As the cells increase in number additional supporting stalks are added. The nest I collected has 130 cells. Bingham mentions 40 as the largest number observed in the genus Icaria.

Locality :—Collected from Bombay.

5. ICARIA VARIEGATA, SMITH.

Bigham, Fauna of British India. Hymenoptera, Vol. I.

The specimens of I, variegata, I have, are collected from Bombay. A nest of this has been brought to my notice by the Rev. J. B. Primrose. The nest of I. variegata is however not constructed on the model of that of I. marginata. A sketch of it is given in fig. 3. Mr. M. J. Presswalla informs me that a species of vespa (Vespa cincta) attacks its nest and carries away its young.

Locality :—Collected from Bombay.

6. TRYPOXYLON INTRUDENS, SMITH.

Bigham, Fauna of British India. Hymenoptera, Vol. I.

Green, Spol. Zeyl. Vol. I.

A specimen of this species I possess differs from those of Bingham described in the Fauna volume. Only the furrows of the median segments are striate. The median longitudinal furrow extends along the whole segment. The furrow bears a small pit on the posterior half of that segment around which the pilose hairs are radially arranged. Black ; the labial palps, the tibiæ and the tarsi of the first pair of legs, the tarsi of the second pair of legs, testaceous brown. The joints of the legs are also coloured slightly testaceous brown.

This species comes inside houses in search of small spiders. It builds its nest with clay on the walls or attached to picture frames etc.

Locality :—Collected from Bombay.

7. TRYPOXYLON PILEATUM, SMITH.

Bigham, Fauna of British India. Hymenoptera, Vol. I.

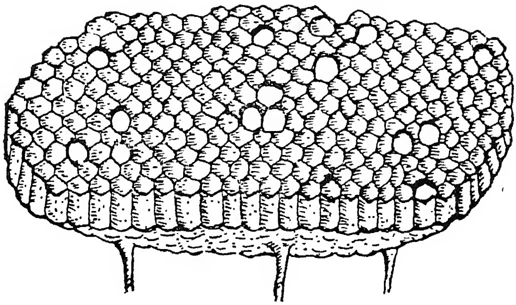

Fig. 2.

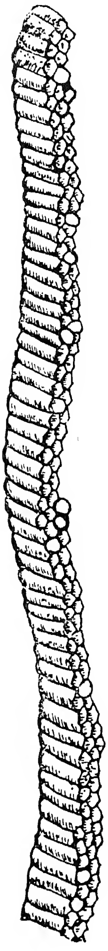

Fig. 3

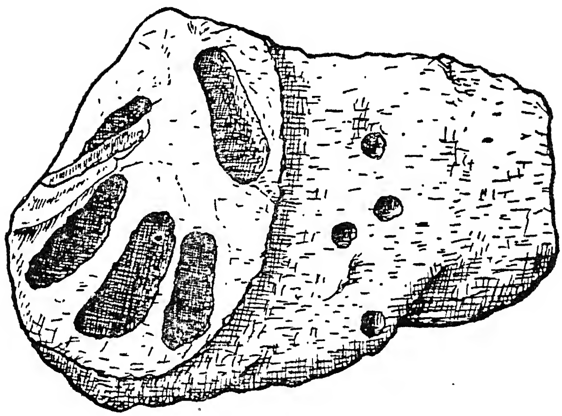

Fig. 1

Description of Figures.

Fig. 1. Nest of Sceliphron Spinolæ Lepel, showing the bottom and one side. The elongated depressions on the bottom surface are the cells. The round holes found on the side are the holes through which adults have emerged.

Fig. 2. Nest of Icaria marginata, Smith. Side view.

Fig. 3. Nest of Icaria variegata, Smith. Side view.

The specimen I have, closely resembles those of Bingham. The habits are similar to those of T. intrudens.

Locality :—Collected from Bombay.

DIMORPHISM AND COAPTATIONS OF THE WINGS OF *SPHÆRODEMA RUSTICUM* Fabr.

By

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Department of Biology, Wilson College, Bombay.

(With 7 text and 3 plate figures)

(*Received 19th December, 1934*)

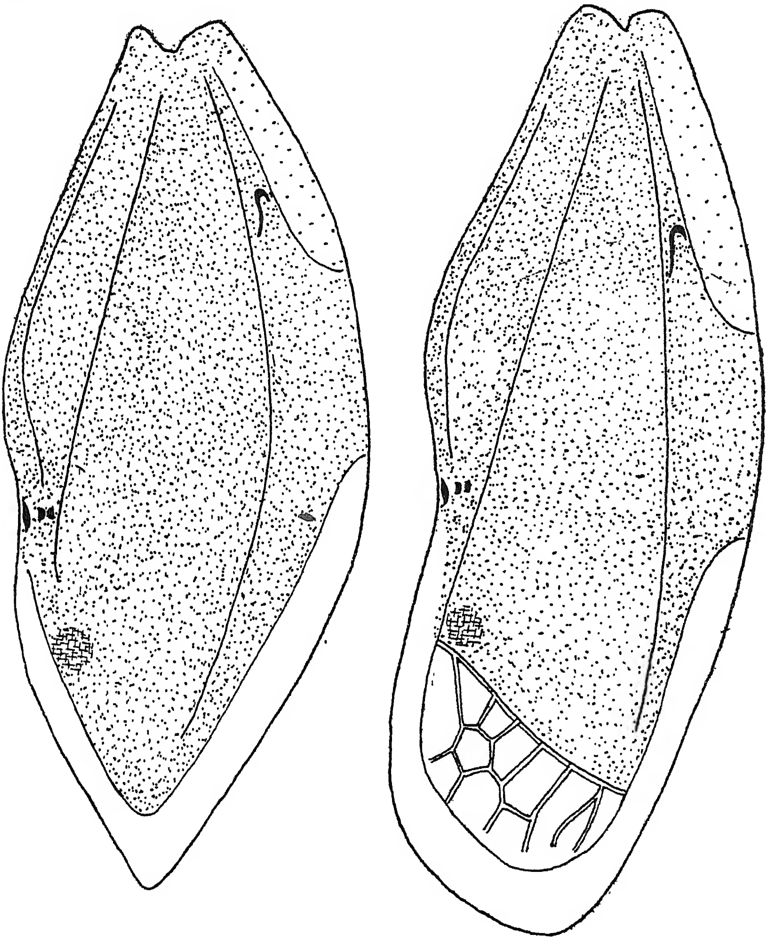
The Sphærodema of the Bombay ponds comprises two kinds of forms. The more common of the two possesses degenerate wings. In this the membranous portions of the hemelytra have become horny and coriaceous (Fig 1. A.) and the anal region has been lost in the hind wings (Fig 2. A.). Together with this degeneration the indirect wing muscles and the apodemes associated with their attachment have also been lost. The other form bears normal heteropterous wings but the wing muscles have become degenerate and modified into the peculiar structures known to morphologists as "tracheo-parenchymatous organs."

Three species of Sphærodema have been recorded from India by Distant (Fauna of British India, Rynchota III. 1906)—*Sphærodema annulatum, S. rusticum* and *S. molestum.* The first of these is easily distinguished from the other two by its definitely larger size and other characters. The other two, *S. rusticum* and *S. molestum,* from Distant's descriptions were found difficult to be distinguished from each other, and Distant's descriptions of both these species are equally applicable to the Bombay specimens. It was therefore necessary to identify our specimens correctly. The chief distinguishing characters given by Distant are the longer tarsal claws of the fore-legs of *S. molestum* and the difference in the size of the two species, *S. rusticum* according to him measuring 15-16 mm. in length and 9-9½ mm. in breadth, while *S. molestum* being 13½-17½ mm. long and a little broader than *S. rusticum.*

The specimens of Sphærodema collected here showed varying sizes from 15 to 19 mm. in length and from 8½ to 11 mm. in width. The largest specimens collected were 19 x 11 mm. and the smallest 15 x 8½ mm., while the intermediate sizes were of all possible combinations: 15 x 9, 15½ x 9, 16 x 9, 16 x 9½, 16 x 10, 16½ x 9, 16½ x 9½, 16½ x 10, 17 x 9, 17 x 9½, 17 x 10, 17 x 10½, 17½ x 9½, 17½ x 10, 18 x 10, and 18½ x 10½, mm. (These measurements were made on a consider-

ably large number of specimens collected during different periods of the year). The difference in size was therefore proved to be of little value in determining the species.

Named specimens of the two species, *S. rusticum* and *S. molestum,* were therefore requested for from different Museums. The



A. B.

Figure 1. Hemelytron. A. degenerate form. B. normal form. X 9.

Imperial Entomologist was kind enough to send a few specimens each, of both *S. rusticum* and *S. molestum.* Both the full winged and the degenerate winged forms, recorded above were included amongst the specimens named *S. rusticum* as well as those named *S. molestum.* The anterior tarsal claws of the specimens labelled *S. molestum* showed no difference in length to those of the specimens labelled *S. rusticum,*

and there was no doubt that the specimens were of one species only. Dr. Pruthi of the Indian Museum, Calcutta, who was referred to in this connection, wrote : "We have some specimens of *S. rusticum* and *S. molestum*, but they look very similar to one another. We have not authentically named specimens, therefore, why don't you dissect the genitalia and decide for yourself whether your specimens belong to one or more species."

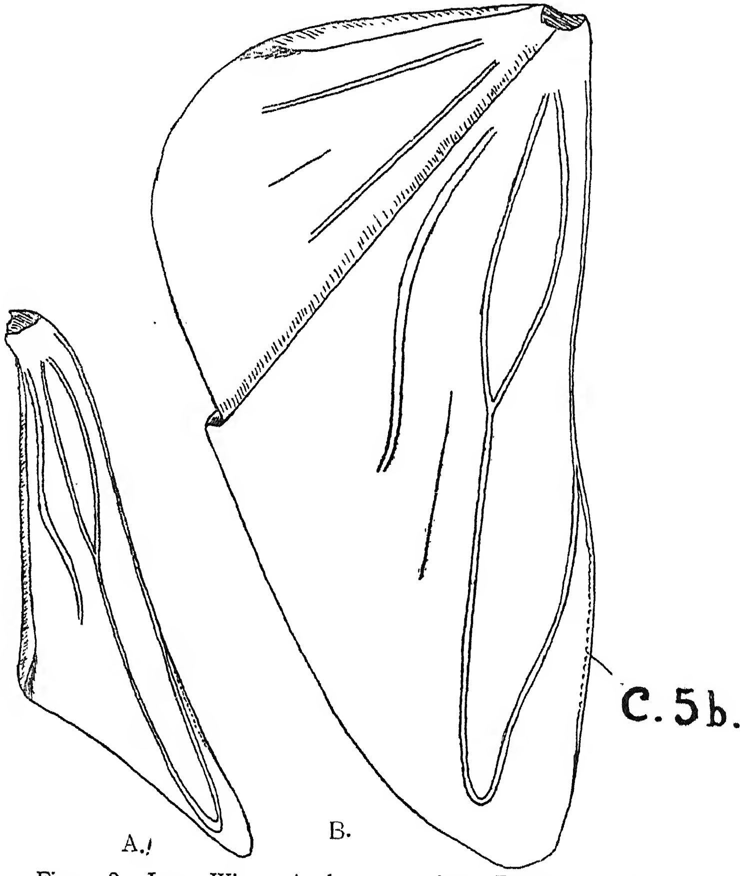


Figure 2. Inner Wing. A. degenerate form. B. normal form. X 9.

A detailed examination of the genitalia and other morphological characters was therefore undertaken and as a result it was found that both the full winged and the degenerate winged forms belong to one species, viz. *Sphærodema rusticum* Fabricius, and this has been confirmed by Mr. W. E. China of the British Museum (Nat. Hist.). If this identification is correct it is doubtful if *S. molestum* is a distinct species ; it is possible on the other hand that it is synonymous with *S. rusticum*.

Alary polymorphism in different families of the Rhynchota is well-known. The phenomenon has been variously co-related with climate, season, mimicry, mode of life, etc., by different investigators (vide Imms, p. 335). But the various kinds of alary polymorphism described by them are those involving reduction of the size of the wings, especially of the hemelytra, such as macropterism, apterism, brachypterism and micropterism. None of these terms however is strictly applicable to the condition found in *Sphærodema rusticum* in which the second pair of wings has lost the anal portion while the rest of the portion has become reduced in size.

The exact significance of the occurrence of alary polymorphism has not so far been ascertained. Temperature and nurture have been regarded as factors influencing the production of alary polymorphism. According to the nurture theory, abundance of food supply tends to produce brachypterous and apterous forms while lack of food will produce macropterous form. But nymphs of Sphærodema collected at different times of the year and kept in the laboratory aquaria for several days without food have moulted into adults with degenerate wings. According to the temperature theory, constantly high temperature tends to produce brachypterous and apterous forms while low temperatures tend to accentuate the production of the macropterous form. This is also not applicable to Sphærodema. In the coldest months of the year (although in one year the macropterous form did predominate) the degenerate winged form was found in large numbers.

Poisson's experiments on Gerris have proved that in that insect temperature and nurture do not determine the wing developments : "Le facteur nourriture et le facteur température ne paraissent pas jouer un rôle déterminant dans l'apparition des formes macroptères, brachyptères et aptères chez les *Gerris*".

Explanation for the occurrence of alary polymorphism as found in Sphærodema and Gerris has to be sought in other ecological factors. Morphological observations indicate that rarely specimens of *Sphærodema rusticum* have the faculty of flight. Three individuals were actually collected while on their wings and examination of their indirect wing muscles revealed normal structure. Besides, a few full winged individuals escaped from the laboratory aquaria from which they could not possibly have crawled out, and were captured later from the laboratory. These facts indicate that some of the full winged individuals still retain the power of flight. Ferrière and Poisson have observed individuals of Nepa in which the wing muscles have not be-

come degenerate but present normal form. This would indicate that such individuals could perform short flights as observed in the case of *S. rusticum*.

THE COAPTATIONS OF THE WINGS.

The sub-elytral space in Sphærodema is used for the purpose of holding air and the hemelytra are therefore firmly fitted to the body and can only be separated from it with some force. They are also interlocked with each other. The locking arrangements or coaptations are brought about in the following ways :

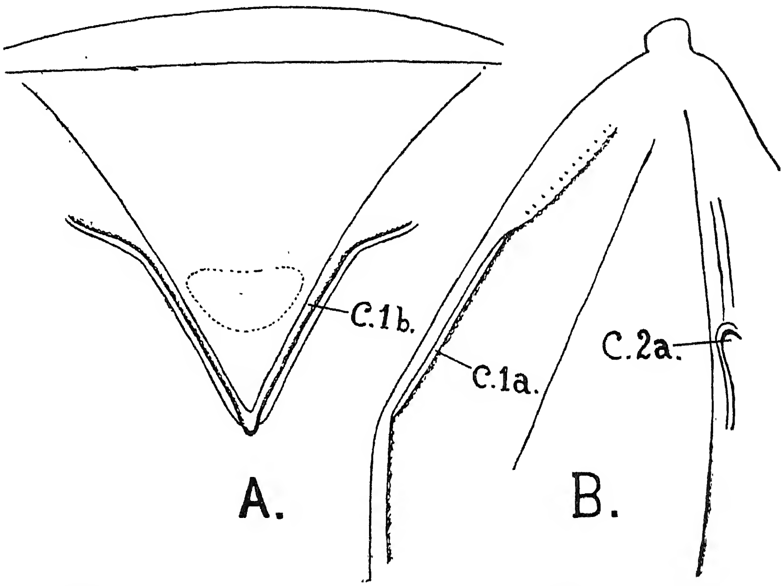


Figure 3. Coaptation No. 1 A. scutellum. B. portion of hemelytron. X 13.

Locking of the Hemelytra to the Body.

Coaptation No. 1.—The margin of the clavus bears a ridge (C. 1a., Fig. 3. B.) which fits into the groove (C.1b., Fig. 3. A.) on the side of the scutellum.

In transverse section (Plate 1. Fig. 8.) both the groove on the scutellum and the ridge on the hemelytron show tubercular protruberances of the chitinous walls which help to take a firmer grip.

Coaptation No. 2.—On the ventral surface of the hemelytron between the embolium and the corium is a socket (C. 2a., Fig. 4. B.) into which the button (C. 2b., Fig. 4. A.) borne by the posterior margin of the upturned meso-pleuron fits in the fashion of a "press-

button." In addition to this the margin between the corium and the embolium is grooved and into this the margin of the meso-pleuron rests. Cuénot et Poisson (1922) and Hamilton (1931) have noted such a "press-button" coaptation in Nepa.

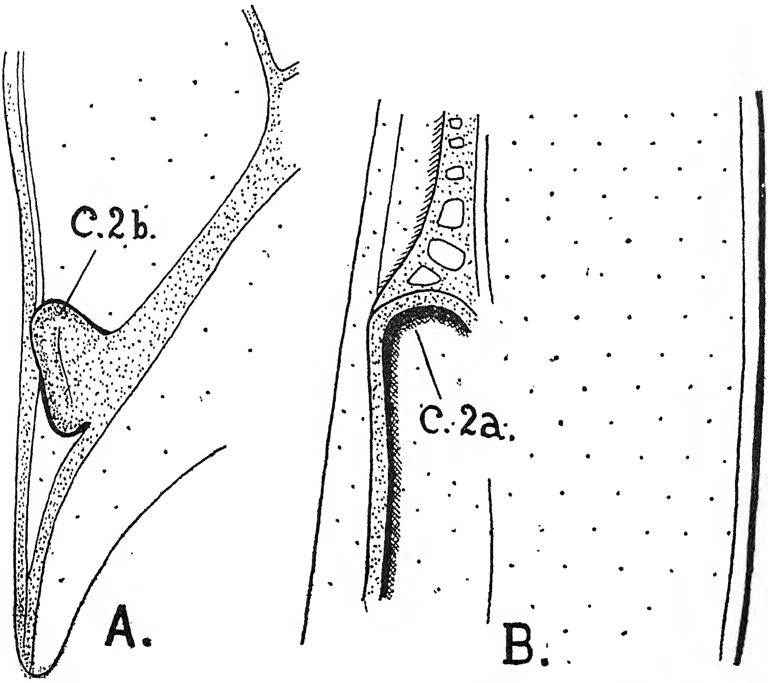


Figure 4. Coaptation No. 2. (Press-button). A. portion of meso-epimeron. B. portion of hemelytron. X 42.

The walls of both the button and the socket show chitinous protuberances similar to those mentioned above (Plate 1. Fig. 9.).

Besides these locking arrangements the hemelytra are locked to each other.

Locking of the Hemelytra to each other.

Coaptation No. 3.—On the posterior angle of the clavus on the dorsal surface is a small elongated chitinous projection. This projection forms a notch facing the opposite hemelytron on which a similar arrangement is present (C. 3., Fig. 5.). When the hemelytra are interlocked the projection on the one fits into the notch on the other. Tubercular protruberances of chitin on the projection and that part of the margin of the hemelytron which forms the notch (C. 3., Fig. 6.) help to render the locking arrangement extraordinarily efficient.

Coaptation No. 4.—A little behind the above interlocking arrangement, can be noticed a reddish spot (C. 4., Fig. 5.) on the posterior inner angle of the corium. This pterostigma bears numerous short

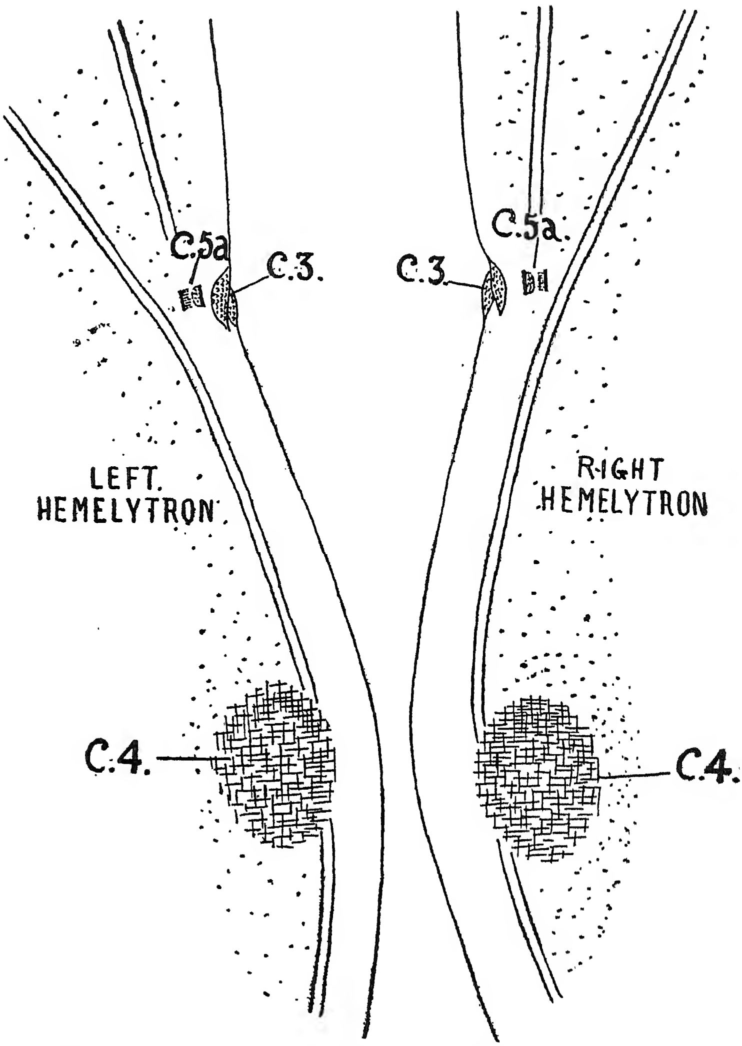


Figure 5. Portions of hemelytra showing Coaptations Nos. 3, 4, & 5. X 32.

stout spines regularly arranged on both the dorsal and ventral aspects. The dorsal spines point backwards towards the apical margin, while the ventral spines are directed towards the costal margin. (Fig. 7.). Such an arrangement is found on both the hemelytra. When the hemelytra are folded, these areas overlap each other and the spines on

the ventral side of the upper hemelytron interlace with the dorsal spines of the lower hemelytron. As the two sets of spines are at

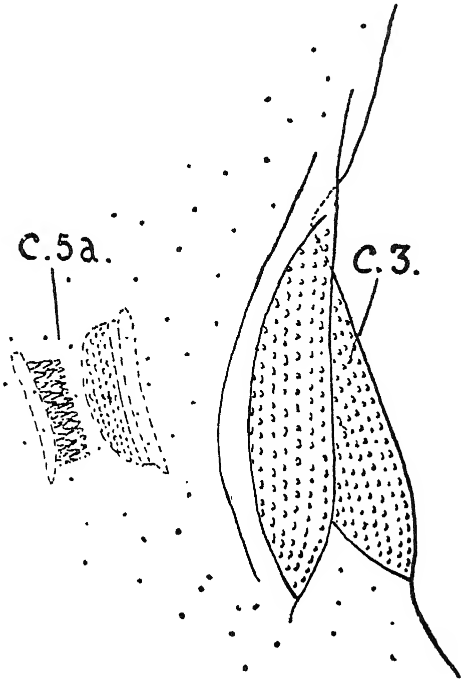


Figure 6. Coaptations Nos. 3 & 5. X 200.

right angles to each other a hold is established. (Plate-Figure 10 shows a cross section of the hemelytron through this interlocking region.)

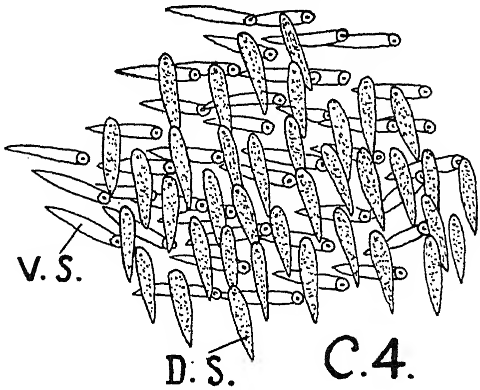


Figure 7. Coaptation No. 4. X 200.

Both these interlocking arrangements are workable whether the right hemelytron is folded on the left, or the left folded on the right,

A fifth coaptation exists for coupling the hemelytra with the membrane wings when in flight. But as most individuals of this species have lost the power of flight the mechanism is of no use to them.

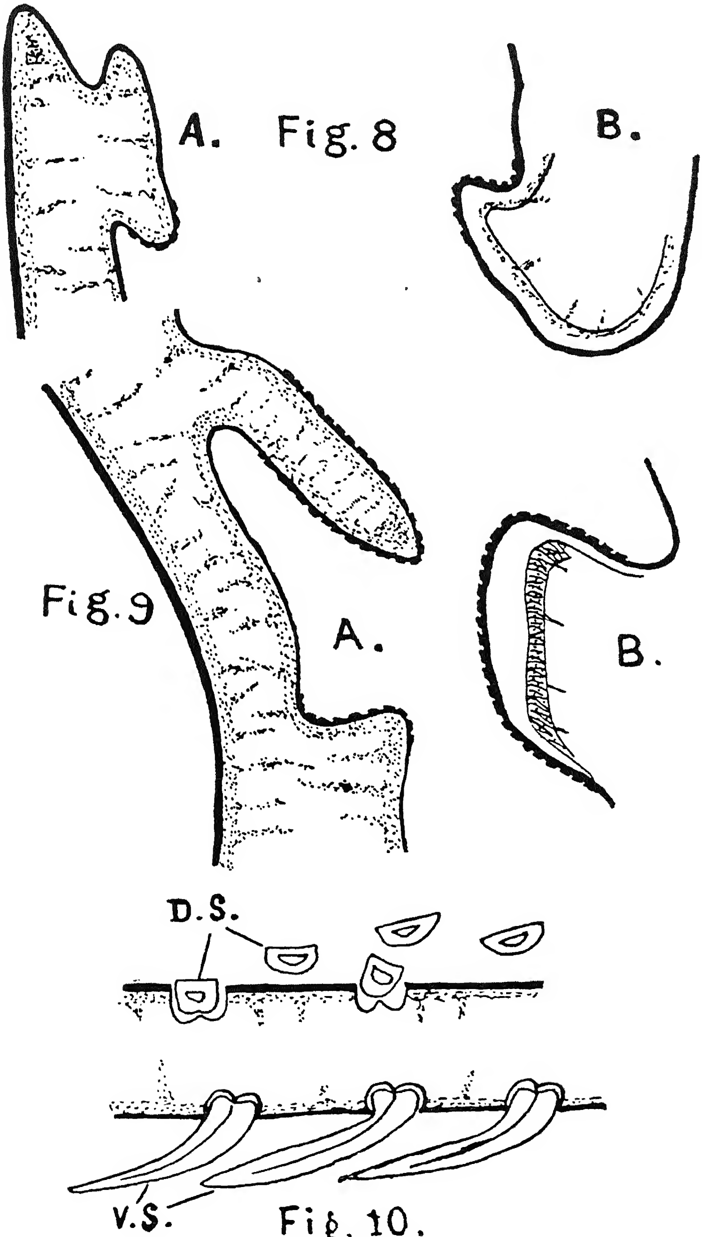
Locking of the Hemelytra to the Membrane Wings in Flight.

Coaptation No. 5.—Close to the interlocking mechanism No. 3, described above, on the ventral surface of the posterior angle of the clavus are found two small longitudinal parallel projections (C. 5a., Fig. 5.). These serve as a catch for the dorsally curved costal margin of the second pair of wings in flight. Of the two projections, the one nearer the inner margin is rounded on the side facing the other and bears tubercular protruberances of chitin. (C. 5a., Fig. 6). The other projection is situated close to the first and bears rows of sharp chitinous dentitions of different lengths, all pointing towards the first projection, (C. 5a., Fig. 6.). When the wings are held in the position of flight the costal margin of the membrane wing which is curved upwards and slightly dented (C. 5b., Fig. 2. B.) can be fitted into the parallel projections on the front wing.

The significance of the first four locking arrangements of the hemelytra is clear when the respiratory mechanism of the insect is properly understood. The insect carries air in the sub-elytral chamber for breathing under water. To render the sub-elytral space an efficient air chamber it is necessary that the hemelytra are firmly held together, and tightly apposed to the sides of the body.

Of the other water bugs examined we found that none of them possesses the interlocking mechanism No. 4. Belostoma which is an actively flying insect can do without this as it has to open its wings for flight very often. It possesses all the other coaptations found in Sphærodema. The arrangements in *Sphærodema annulatum* are like those of *Belostoma indica.* Perhaps this species still retains the power of flight to a very great extent as does Belostoma. In insects belonging to the family Nepidæ (*Nepa cinerea, Laccotrephes elongatus. L. grisea,* and *Ranatra*) the hemelytra are locked posteriorly to the margin of the abdomen by a groove and ridge arrangement. Considering the elongated shape of their bodies and the fact that in them the sub-elytral chamber is shallow though somewhat deep towards the margins of the abdomen, this locking of the hemelytra along the abdomen seems more suited to them.

All these insects mentioned above possess the wing coupling apparatus No. 5. Some of the well-known instances of the wing coupling arrangements are found in the Hymenoptera and Lepidoptera. Poisson (1922) noted the wing coupling apparatus in the Heteroptera, but about the interlocking of the hemelytra he wrongly asserted ;



SPHÆRODEMA RUSTICUM

Figure 8. Section through Coaptation No. 1. A. inner margin of the clavus. B. margin of the scutellum. X 150.

Figure 9. Section through Coaptation No. 2. A. socket on the hemelytron. B. button on the meso-pleuron. X 150.

Figure 10. Section through Coaptation No. 4. X 700.

" Il n'existe pas chez les Hémiptères d'appareil d'accrochage entre les élytres analogue à celui que l'on peut observer chez les Coléoptères". Hamilton also failed to note the locking mechanisms Nos. 3 and 5 in *Nepa cinerea.*

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LETTERINGS.

C. 1a. Coaptation No. 1—Curved margin of the clavus.
C. 1b. Coaptation No. 1.—Groove on the scutellum.
C. 2a. Coaptation No. 2.—Socket on the hemelyton.
C. 2b. Coaptation No. 2.—Button on the meso-pleuron.
C. 3. Coaptation No. 3.—Interlocking protruberances on posterior angle of the clavus.
C. 4. Coaptation No. 4.—Cpinous interlocking of the hemelytra.
C. 5a. Coaptation No. 5.—parallel protruberances on the hemelytron.
C. 5b. Coaptation No. 5.—Curved costal margin of the wing.
D. S. Dorsal Spine.
V. S. Ventral Spine.

THE DEVELOPMENT OF THE FEMALE EFFERENT GENITAL DUCTS IN APIS INDICA

By

C. J. GEORGE AND JOHN A. MULIYIL

(With 2 text- and 17 plate-figures.)

(*Received 3rd January, 1935.*)

The homologies of the genitalia and genital ducts in insects have recently attracted considerable attention. Christophers traced their development in Diptera, Singh-Pruthi in Homoptera and Coleoptera, George in Homoptera and Zygoptera, Nel in Orthoptera, and Metcalfe in Coleoptera, Homoptera and Diptera. As a result, the older views on the nature of these organs have been considerably modified. It is not proposed to give a full historical review of the earlier work here since it has been done by the above mentioned authors. While there is observed little variation in the development of the male genital ducts, there is considerable diversity in that of the female genital ducts of the various groups. Regarding the oviducts Singh-Pruthi found that except for a short stump the rest of the efferent system in *Tenebrio molitor* is ectodermal in origin. Metcalfe working on *Sitodrepa Panicea* and others supported his conclusions. Zander found that in *Apis mellifica* there is an encroachment of ectodermal cells from the ectodermal region of the oviducts to replace the mesodermal cells of the paired oviducts during development. Nel working on Orthoptera, though he himself could find no support for Zander's view, was convinced that there was such a possibility. Zander's view found further support from Metcalfe in her work on *Dasyneura leguminicola.* In Homoptera and Zygoptera George found no evidence of such migration.

The present piece of research was undertaken in the belief that a study of the development of these organs in Hymenoptera will further enlighten us on the subject. The chief work on the female genital ducts in Hymenoptera is that of Zander. His results could be summarised as follows :

(1) The common oviduct arises from behind the 7th abdominal segment and gets secondarily shifted to the 8th segment.

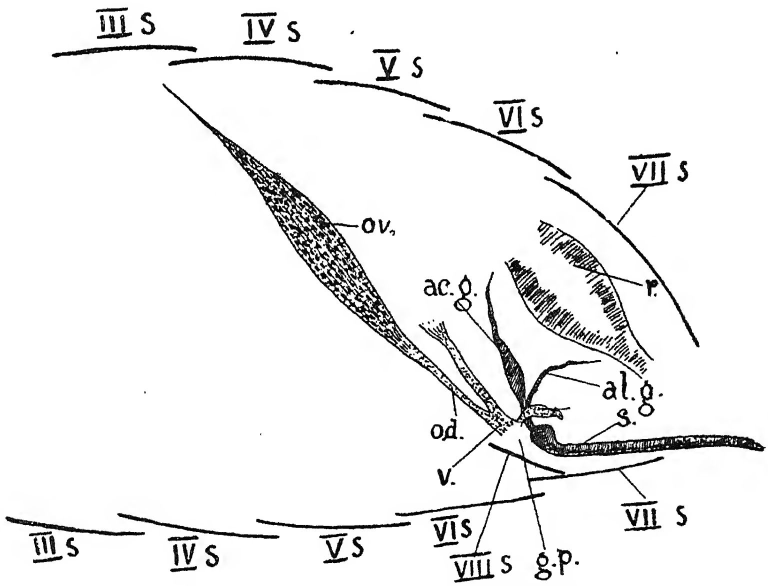
(2) The spermatheca originates in a pair of rudiments from behind the anterior ovipositor lobes.

(3) The acid gland takes its origin as an unpaired rudiment from between the inner ovipositor lobes.

(4) The paired oviducts are hypodermal in the adult, the original mesoderm having been replaced by the ectoderm.

THE ADULT FEMALE ORGANS OF *Apis indica.*

The female organs of the worker bee are similar to those of the queen in all important respects. The ovaries are however very much smaller than those of the queen and the ovarioles are fewer in number. They are covered by a thin layer of connective tissue coat. They are situated in the 3rd to the 5th abdominal segments. Each ovariole is a long thin tube not unlike those of other insects and consists of a single layer of cells. Anteriorly the ovariole tapers to a solid cord. The anterior tapering cords of the ovarioles are bound together into a bundle in each ovary. The binding connective tissue strands are continued anteriorly and attach the ovaries to the dorsal wall. Posteriorly the lumen of the ovariole is larger and there con-



Text-figure 1. Diagrammatic lateral view of the adult female organs of a worker bee.

tains eggs in different stages of development, the posteriormost ones being the most advanced. In the worker bee the eggs are in an arrested state, since the worker does not lay eggs unless the queen is destroyed. There is considerable variation in the relative development of the ovaries in different workers, and it was noted that only a few workers in a hive could lay eggs if and when the occasion arises.

Each of the ovaries opens posteriorly into a somewhat wide oviduct. The oviducts enlarge towards their distal extremities and open into a single wide tube, the common oviduct. The posterior part of the common oviduct functions as the vagina. The inner layer of the vaginal tube is thrown into folds and so much so the lumen appears narrow in transverse sections. The vagina opens into a copulatory pouch. Dorsal to the vaginal opening is situated the opening of the spermatheca. Into the posterior part of the copulatory pouch fits the base of the sting. Text-figure 1 shows the relative positions of the various organs.

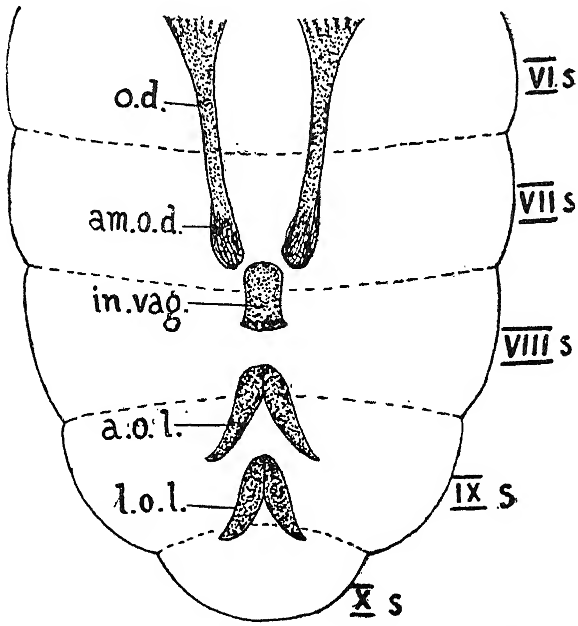
THE DEVELOPMENT OF THE EFFERENT GENITAL DUCTS.

The worker larva of *Apis indica* when fully grown is 10 mm. long. It is yellowish brown in colour, this colour being due to the presence of pollen grains and other matter found in the midgut. The midgut is abnormally swelled up with fæcal matter and occupies more than $\frac{3}{4}$ of the length of the body. At this stage the reproductive system consists of the ovaries and the oviducts and three rudiments in connection with the hypodermis of segments 7, 8, and 9, which later on will develop as invaginations of the common oviduct, the spermatheca, and the acid gland respectively. The ovaries are situated dorso-laterally to the alimentary canal. They are surrounded by a coat of fibrous tissue, the ovarian stroma. The oviducts are thin solid cords which after piecing the ovarian stroma take an obliquely ventral course on either side of the alimentary canal and terminate on the hypodermis of segment 7, on either side of the 7th abdominal ganglion. The blind posterior regions of the oviducts are very much enlarged.

The buds of the gonapophyses are seen as small projections beneath the larval cuticle on segments 8 and 9. On the mid-ventral line is a dimple on the anterior edge of segment 8, the already mentioned rudiment of the common oviduct. A sagittal section of the larva will reveal that it is the rudiment of an invagination. The second rudiment exists between the rudiments of the anterior ovipositor lobes on the hind region of segment 8. This is not externally visible as the rudiments of the ovipositor lobes cover it, whereas the former is seen clearly. The third rudiment exists on the 9th sternum and like the preceding one is not externally noticeable as the ovipositor rudiments cover it.

After the larva completes its feeding stage the cell is capped. Soon after, the larva defaecates and gets rid of the fæcal matter accumulated in the midgut. As a consequence the walls of the midgut collapse and the larva as a whole undergoes a change in size. It

then spins a cocoon preparatory to entering on the pupal stage. Its yellowish brown colour changes into a clear white. The important changes connected with the early stages of metamorphosis now become manifest. The larval fat body shows signs of disruption. The mid-gut which has collapsed into a thin cord with practically no lumen now shows a cellular organisation in which the cells are less definite. The imaginal buds of the hypodermis begin to grow quickly. The beginnings of the elongation of the hypodermal rudiments of the genital ducts are also seen at this stage. Text-figure 2 gives a ventral view of the organs at this stage. The dimple behind segment 7 elongates anteriorly. The rudiment on the 9th sternum elongates dorsad. The



Text-figure 2. Ventral view of a pupating lavra showing abdominal segments VI-X. The position of the hypodermal rudiments and the oviducts are shown.

rudiment behind the 8th sternum also shows development though not to such a marked degree as in the case of that on segment 9. In the mid-ventral line of the 8th and the 9th sternum is developed a groove (the genital groove) into which open the three invaginations. The groove is wide at the anterior region and narrows towards the posterior region.

THE VAGINA

Plate-figures I and II illustrate the early stages in the development of the vagina. The rudiment of the vagina which is already pre-

sent in the beginning of the metamorphosis grows anteriorly. Fig. I shows its open lip and Fig. II shows the anterior limit of the invagination which abuts against the distended extremities of the oviducts. The vagina at this stage is very short and extends only to a short distance from the anterior limit of the 8th segment to the posterior region of the 7th segment. It still retains its relation with the hypodermis.

As further development proceeds the vagina extends posteriorly. Growth at this stage is very active at the vaginal lip. The whole extension of the vagina to the posterior limit of the 8th segment is so sudden that it is difficult to procure the exact stages. The exact mode of this extension is not certain. Most probably that part of the genital groove behind the vaginal opening is converted into a tube. It might be also, as Nel has described in Orthoptera, due to growth of the vaginal lip posteriorly. Or it might be as a result of both kinds of growth. However, when the development is complete the vagina extends to the posterior limit of the 8th segment. Anteriorly the vaginal invagination undergoes important changes. Its anterior extremity becomes flattened and a median longitudinal constriction appears on the dorsal and the ventral surfaces. As these deepen the dorsal and ventral walls meet along this line and ultimately the vagina is split into a right and a left tube. This split extends posteriorly to a short distance. When the development is complete these two ducts become intimately associated with the oviductal extremities of the respective sides. Plate-figures III—VII are of sections passing through the posterior region of the 7th and the anterior region of the 8th segment. Fig. III shows the blind extremities of the two ducts into which the vaginal invagination divides and the blind extremities of the oviducts. Fig. IV shows traces of the extremities of the oviducts and the ends of the two ducts derived from the vaginal invagination. Figs. X and XI show the same structures in longitudinal sections.

The later development consists of the fusion of each of the oviducts with the duct of its side derived from the vagina. This fusion establishes the efferent passage.

THE SPERMATHECA.

The spermathecal rudiment originates on the 8th segment from the genital groove immediately behind the rudiments of the anterior ovipositor lobes. It grows posteriorly, its opening being therefore directed somewhat cephalad. It is very much narrower than the vaginal invagination. Plate-figures XII—XV are of transverse sections passing through the region of the spermatheca and show its position. As further development proceeds the spermathecal inva-

gination becomes more approximated to the vagina and in the adult it comes to lie on the dorsal aspect of the genital pouch. Figs. VIII, IX and X also show the relation of the spermatheca to the vagina.

The Accessory Glands.

The rudiment of the invagination noted on the 9th segment of the larva elongates during prepupal stages. Plate-figures XVI and XVII show the disposition of this invagination at the early stages. Anterior to it develops a small invagination from the genital groove. Figs. VIII and IX show this invagination. This invagination shows a narrow lumen and thick columnar wall. This is the rudiment of the alkaline gland. During the later stages the acid gland widens out into a sac a short distance from its opening. At the distal end the lumen is narrow and the gland consists of a long coiled tube. The sac develops into the reservoir of the gland.

Discussion.

The vagina and the female opening.—Both Wheeler and Heymons found that the female opening in the embryonic stages of Orthoptera was situated behind the 7th segment. This is incompatible with what is obtained in the adult in which the female opening is found behind the 8th segment. The findings of Wheeler and Heymons were therefore not thoroughly accepted. Zander showed in Hymenoptera that during the course of post-embryonic development the vaginal opening found behind the 7th in the embryo becomes secondarily shifted behind the 8th. George showed in 1928 that in Homoptera the female opening placed behind the 7th in the early nymphs is shifted gradually towards the 8th sternum during the later stages. These findings on the backward shifting of the gonopore was supported by Nel (1930) who in Orthoptera found an almost identical development. Recent work of Metcalfe on Homoptera, though it confirms the original conclusions of George, shows that the shifting of the gonopore takes place as a result of the coalescence of the spermathecal invagination with the vaginal. From observations on Melipona which has a spermatheca independent of the vagina in the adult condition George (1934) concluded that in development there is a backward growth of the vagina from the anterior region of the 8th segment to the posterior region of that segment along the genital groove. From a reexamination of his slides of Philaenus and from viewing the process in the light of the more recent work of Metcalfe we find that the development of the vagina and the spermatheca does not follow the same rate in different individuals. In some specimens the spermatheca grows more vigorously than the vagina and in others an opposite condition is found. In the Homopteran Philaenus the spermatheca

extends forwards on the dorsal aspect of the vagina and in specimens of the first category mentioned above the coalescence of the vagina and the spermatheca takes precedence over the extension of the former posteriorly. As a result, the posterior extension of the vagina so clearly manifested in specimens in which the spermatheca grows very slowly, is rendered obscure. In *Apis indica* the spermatheca extends backwards and there is no chance of the early fusion of the spermatheca and vagina. We have no hesitation therefore to maintain that in Apis as in Philaenus there is a backward extension of the vagina along the genital groove as a result of which the female genital opening becomes placed at the hind region of the 8th segment.

The spermatheca.—Zander showed that the spermatheca originates from paired rudiments. We do not find any support for his contentions nor have workers on the other groups found grounds to agree with him. In Diptera and Coleoptera the spermatheca arises from the 9th segment and in Orthoptera, Homoptera and Hymenoptera from behind the 8th segment. Singh-Pruthi who worked on Coleoptera criticises Jackson for ascribing the spermathecal opening to the 8th segment. Nel who worked on Orthoptera is equally vehement in condemning Singh-Pruthi's conclusions. He considers the Coleopterous condition as exceptional. The study of development in Homoptera, Hymenoptera, Coleoptera, Lepidoptera, and Diptera shows that there are two invaginations, one arising from behind the 8th and another from behind the 9th. In those groups of insects in which the female opening is behind the 8th the one near it develops as the spermatheca. In the other groups of insects in which the female opening is behind the 9th the spermatheca is developed from the 9th. George in his paper on Homoptera raised the question whether the invagination behind the 9th segment had originally a spermathecal function or served as an accessary gland. From the evidence now available we are inclined to believe that primitively insects had spermatheca on segments 8 and 9 and possibly on 7 also. With the shifting of the gonopore to the 8th segment the spermatheca behind the 8th was strengthened and the one behind the 9th gradually became modified into an accessary gland ; with the shifting of the gonopore to the 9th, the one behind the 8th was absorbed to form the oviduct and the one behind the 9th became developed as the spermatheca. The condition obtained in Blatella may be regarded not as the most primitive but as a degenerate condition.

The alleged displacement of the mesoderm by the ectoderm in the genital ducts.—In many groups the mesodermal oviducts are found to terminate in the early stages on the 7th abdominal segment without any signs of degeneration. (Vide Nel's review of the earlier work on

p. 59,) Zander, Singh-Pruthi and Metcalfe found that there is marked encroachment of the ectodermal cells from the oviductal or uterine invagination as the case may be, to the mesodermal oviducts. Zander observed that during the post-embryonic development hypodermal invasion occurred from the vaginal invagination and gradually replaced the mesodermal epithelium of the oviducts. Singh-Pruthi and Metcalfe working on Coleoptera and the latter on Diptera showed that the oviducts are mostly hypodermal in origin. Nel, though he himself found no support to the above conclusions in Orthoptera, was inclined to accept it for insects in general. The writings of Metcalfe seems to imply such an opinion. But at the time of union between the hypodermal and the mesodermal oviducts in Apis we do not find any degeneration in the mesodermal oviducts. Whether after the union the ectodermal tissue extends anteriorly to displace the mesodermal epithelium we have not been able to determine. It is therefore premature at this stage to conclude that there is an encroachment of ectodermal cells in the domain of the mesoderm in the oviducts in insects in general.

Summary and Conclusions.

I. The oviducts in the larva of *Apis indica* reach the hypodermis of the 7th abdominal segment. The vagina arises as a median invagination behind the 7th. It gets secondarily shifted to the 8th by the gradual growth of its ventral lip. Anteriorly it divides into two and each of these divisions joins the respective oviduct of its side.

2. The spermatheca arises as an invagination from behind the 8th. It gets later on fused with the vagina and ultimately comes to open on its dorsal wall.

3. An invagination between the inner ovipositor lobes on the 9th segment develops into the acid gland. Later on the alkaline gland arises as a smaller invagination a little anterior to the acid gland.

4. From the variable position of the spermatheca it is postulated that primitive insects possessed spermatheca on segments 8 and 9 and probably on 7 also. Some groups retained that on the 9th and others that on the 8th.

5. There is no evidence to suppose that there is a degeneration of the mesodermal oviducts in insects in general nor is there sufficient ground to hold that there is a later displacement of the mesodermal epithelium by the ectoderm in insects in general.

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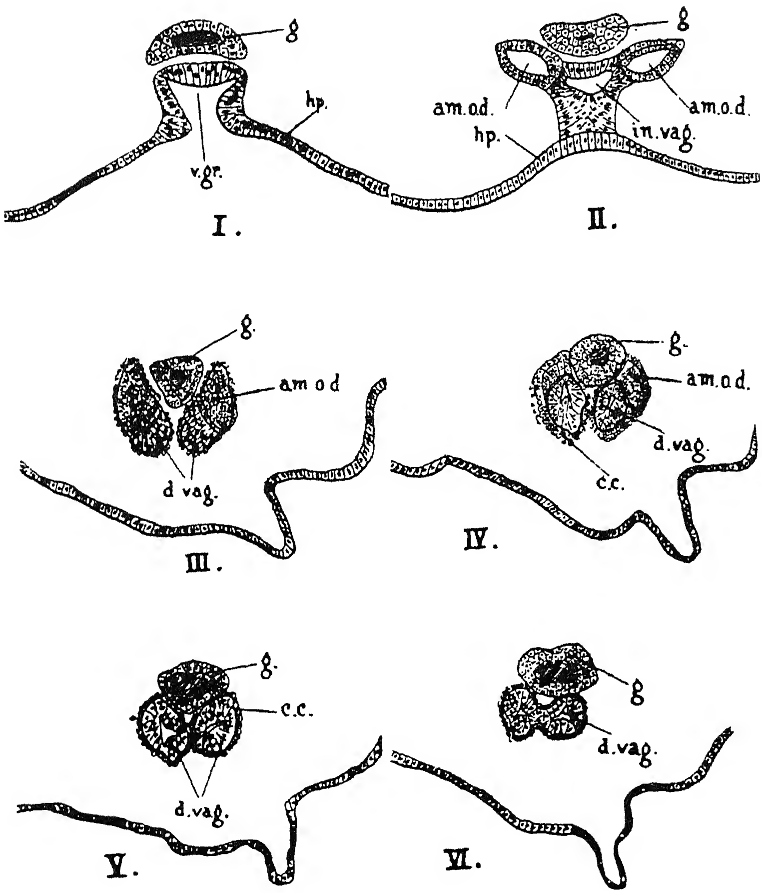
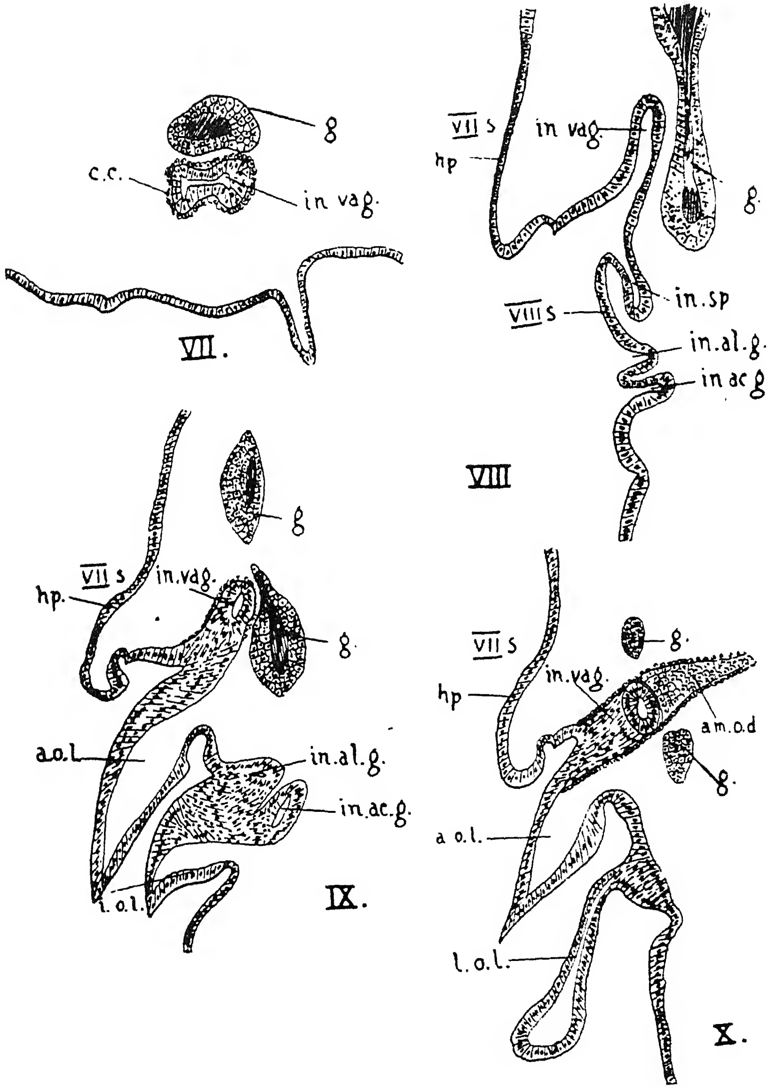


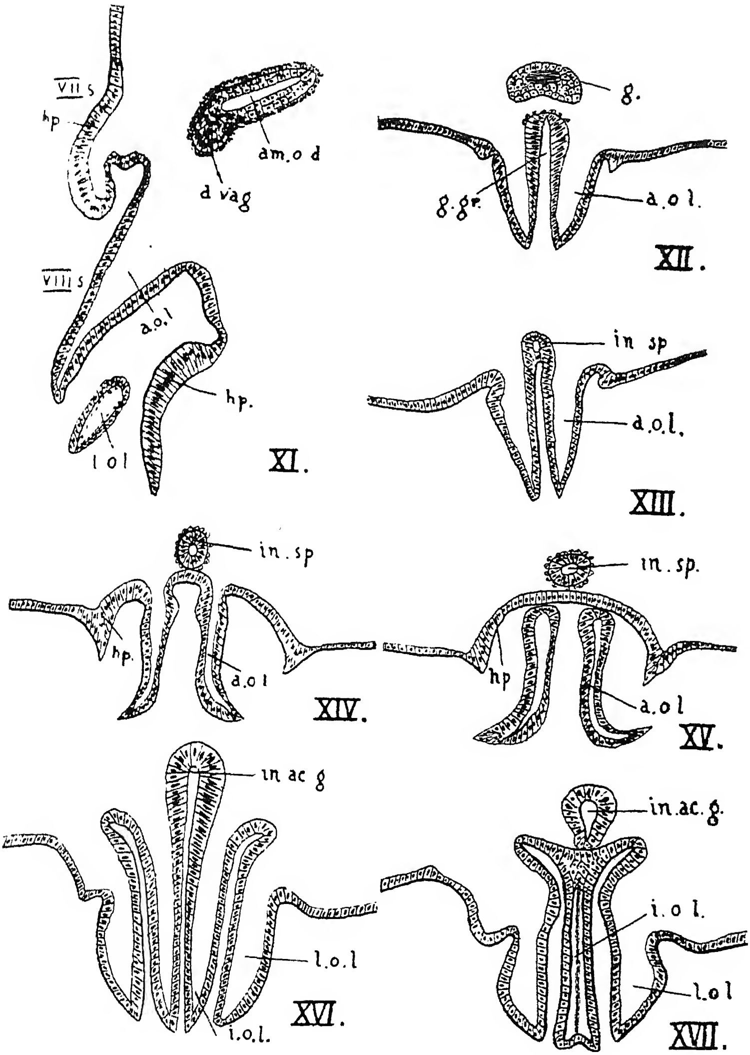
Fig. I. T. S. through the VIIth abdominal segment. It shows the vaginal rudiment and the extremities of the oviducts.

Fig. II. T. S. through the anterior region of the abdominal segment VIII. It shows the groove into which the vagina opens behind.

Figs. III-VII. T. S. through the abdominal segments VII and VIII. III shows the two divisions of the vaginal invagination and the extremities of the oviducts. IV. shows stump of the oviducts and the ends of the divisions of the vaginal invagination.



Figs. VIII-XI. Vertical longitudinal sections through the VIIth VIIIth and IXth abdominal segments, showing the growth of vagina, the acid gland, alkaline glands and the spermatheca.



Figs. XII-XV. T. S. through the VIIIth and IXth abdominal segments showing the development of the spermatheca. XII shows the spermatheca opening into the genital groove. XIII posterior to section XII, just before the spermatheca opens. XIV and XV posterior to section XIII.

Figs. XVI and XVII T. S. passing through the IXth abdominal segment. XVI shows the opening of the acid gland into the genital groove. XVII section posterior to XVI.

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Letterings

ac. g.—acid gland.

al. g.—alkaline gland.

am. o. d.—enlarged extremities of the oviducts.

a. o. l.—anterior ovipositor lobe.

c. c.—connective tissue cells.

d. vag.—divisions of the vaginal invagination.

g.—ganglion.

g. p.—genital pouch.

g. gr.—genital groove.

hp.—hypodermis.

in. ac. g.—invagination of the acid gland.

in. al. g.—invagination of the alkaline gland.

in. sp.—invagination of the spermatheca.

in. vag.—invagination of the vagina.

i. o. l.—inner ovipositor lobe.

l. o. l.—lateral ovipositor lobe.

o. d.—oviduct.

ov.—ovary.

r.—rectum.

s.—sting.

v.—vagina.

v. gr.—vaginal groove.

IIIs, IVs, Vs, VIs, VIIs, VIIIs, IXs.—3rd, 4th, 5th, 6th, 7th, 8th and 9th, abdominal segments.

OBSERVATIONS ON *GLOMERELLA CINGULATA* (STONEMAN) S. & V. SCH.

parasitic on *Tinospora cordifolia* Miers.

(With two plates)

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Tinospora cordifolia Miers, a plant much used in Indian medicine, grows wild on hedges at Ahmedabad. Its leaves harbour a number of fungi as parasites, occurring in the conidial, pycnidial and perithecial stages. The most conspicuous of these is a conidial form (a *Cercospora*) which produces well defined leaf-spots bearing white conidial tufts on the lower surface and a perithecial stage which appears regularly to follow it on fallen and decomposing leaves. A genetic connection between these two was hence suspected and an investigation was undertaken to settle the point.

During the course of this investigation another conidial form (a *Colletotrichum*) and a pycnidial form (a *Phoma*) were also found to occur along with the *Cercospora* and it became necessary to investigate the mutual relationships, if any, of all these various forms of fungi occurring in such close association on the same host and in the same part of it. These forms have been identified in consultation with the Imperial Mycologist, Pusa and Dr. H. Sydow of the Annales Mycologici, Berlin, as follows :—

(1) The conidial form causing well defined white spots on leaves—*Cercospora Tinosporae* Syd.

(2) A pycnidial form succeeding (1) on still living leaves—*Phoma* sp. (according to the Imperial Mycologist), *Phyllostictina* sp. (according to Sydow (8).)

(3) Another conidial form, not associated with any definite spots but occurring all over the leaf—*Colletotrichum* sp.

(4) An ascigerous stage in the form of black perithecia occurring on leaves spotted with *Cercospora* which have fallen and are decaying—*Glomerella cingulata.*

Cultural and inoculation studies were carried out with each one of these forms with the result that it was found that there are at least two distinct fungi occurring together in the leaves of *Tinospora cordifolia*. While the ascigerous stage has been proved to have no connection with the *Cercospora* as first suspected, a complete proof of the genetic connection between the *Glomerella* and the *Colletotrichum* has been obtained once again. A strong indication of a genetic connection between the *Phoma* or *Phyllostictina* and the *Cercospora* has been also obtained but some further work is necessary on this point.

This paper presents the results of the part of the investigation of the *Tinospora* fungi which deals with the *Colletotrichum* and the *Glomerella.*

Previous Work

Glomerella with its associated conidial forms, *Gloeosporium* or *Colletotrichum*, has been extensively studied and the genetic connection between its two stages has been repeatedly proved in Europe and America. Barrus (1) writing in 1921 states that "the perfect stages of at least thirty-two other *Gloeosporia* or *Colletortricha* have been found in nature or produced in culture" since the original discovery of this connection in 1898. But, in India, although Butler and Bisby (2) mention a number of hosts for these forms of fungi, they have been studied in detail on only a few of them and the genetic connection between them has been proved only once before and that was by Dastur (3) working with *Glomerella* occurring on chillies and papaya. A detailed account of the same *Glomerella* on an entirely different host would not, therefore, be without interest.

Materials and Methods.

Material of the fungus was available abundantly between the months of August and December in the field. It was preserved in different stages of development in Formalin (4%) and in Juel's fixing solution. This material was studied in free hand sections. For microtome sections, in addition to Juel's solution, Allen's fluid and Allen's modification of Bouin's fluid were used as fixing agents. Haidenhain's Iron alum hæmatoxylin was used for staining.

Germination trials with the spores were carried out in Böttcher's slides. Cultures traceable to single spores were obtained by the usual methods. The nutrient medium usually used was Thaxter's hard potato agar, though others, such as, corn-meal agar, glucose-peptone agar, glucise-meat extract-agar, Tinospora plant-juice agar, Tinospora stem bits and potato plugs, were also tried.

Inoculation experiments were carried out with conidia produced by subcultures from single-spore cultures, leaves of the host, either detached or on cut branches, being used. As regards the inoculations with ascospores of the *Glomerella,* various methods were tried : (1) The over-wintered leaf containing perithecial bodies was first softened with distilled water. It was then spread, damp, on a wire netting upon the leaf to be inoculated. In this way the leaf would be sown with ascospores ejected from the perithecia ; (2) hand sections of perithecia were taken and these were placed on leaves ; (3) Perithecia were broken in a tube containing sterile water and the ascospore-suspension thus obtained was used as inoculum.

Before the inoculation experiments were started it was ascertained that the spores were in a germinating condition by previous germination trials. The leaves to be inoculated were in all cases washed with corrosive sublimate (1 in 1000) solution and rinsed thoroughly afterwards with distilled water. After inoculation they were covered with a bell jar. Controls were kept in all cases.

Observations.

(i) The *Colletotrichum* stage :

The part of the leaf infected with this fungus shows slightly raised dark dots which are seen under the microscope to be acervuli. These are generally arranged in concentric rings but scattered ones are not wanting. They are also found on the veins, particularly at the angles where two veins meet. The fungus not only produces foliar lesions but even the petioles may be badly affected, especially on fallen leaves. No well defined spots, as in the case of the *Cercospora,* are formed by this fungus.

The mycelium of the parasite traverses the tissues of the host and is whitish in colour. In the epidermal and subepidermal cells the hyphæ collect together and develop a pseudoparenchymatous stroma from which the conidiophores arise. (Fig. 1.) The latter are short, hyaline and measure 13-16 μ by 3-4 μ. The conidia are borne singly at the tips of the conidiophores and are one-celled and hyaline, slightly curved and with the ends somewhat pointed. The contents of the spores are granular, with a conspicuous oil globule in the centre. (Fig 2). The spores in the mass are pink in colour and are held together by a white, gelatinous substance. When a mass of spores from an acervulus is placed in water they separate readily and become distributed in the water. They measure 16-17 μ by 3-4 μ.

The acervuli are plentifully supplied with setæ which are dark brown in colour. They are arranged irregularly all over the acervulus.

They are usually straight, sometimes curved, broader at the base and gradually tapering towards the apex, 1-2 septate and measure 60-150 μ by 4-8 μ. The dark colour of the acervuli is due to these setæ.

Spore Germination.

The spores germinate readily in water within a period of 12-14 hours. (Fig 3). Germination usually takes place by the protrusion of a germ tube from one end of the spore only, but it may also arise from the side. In some cases more than one germ tube, as many as three even, have been observed. After attaining a length of two or three times that of the spore, the growth of the germ tube seems to slow down appreciably. There is no swelling or increase in size, nor has any septation been distinctly observed in the germinating spore. In most cases an appressorium is produced at the end of the germ tube. This is a sub-globose body with dark-coloured thick walls and contains granular protoplasm. It is produced at the end of a relatively short hypha. After nearly twenty-four hours an appressorium sends out a very short tube. A secondary appressorium has not been noticed on this tube.

Cultural Studies.

Cultures on Thaxter's potato agar from conidia give on the second day a superficial, pinkish white growth which, later, shows a tendency to turn greenish black. The mycelium looks slightly greenish under the microscope and consists of two kinds of hyphæ, thin in some places and thick in others. It is closely septate and shows numerous vacuoles in the granular protoplasm. Later on, small dark dots develop in the cultures in more or less concentric circles showing a distinct zonation. On microscopic examination these are found to be acervuli with the characteristic dark brown setæ. The setæ are found to be more abundantly produced in artificial cultures than in nature.

After about a fortnight, among the acervuli there appear in some cultures larger black bodies which possess neither setæ nor conidia and are more superficially developed. On crushing these, sometimes, a few spores looking like ascospores of *Glomerella* were seen but they could not be traced to any distinct asci. Cultures were kept for fourteen months and allowed to dry up, but no mature perithecia were obtained.

Cultures obtained on Thaxter's potato agar by sowing a single setae instead of a single conidium gave identical results. No development beyond the formation of immature perithecium-like bodies took place.

Tinospora plant-juice agar, corn meal agar, glucose-meat extract-agar, potato plugs and partially sterilised bits of *Tinospora* stem were tried for the development of the ascigerous stage but without success.

Unmistakable perithecia developed, however, in cultures on glucose-peptone agar round the acervuli dots. They had a prominent beak, a wall composed of pseudoparenchyma and they were developed on a stroma formed by interwoven hyphæ. They showed distinct asci and ascospores inside. (Fig. 4). The measurements of the asci and ascospores agreed with those found on leaves in nature as well as those developed on incubated leaves in the inoculation experiments to be described later.

It will be thus seen that sowings of the conidia (or in some cases of single setæ) gave rise to immature perithecium-like bodies on all the media tried except glucose-peptone agar. On this last medium alone the perithecia were fertile and produced ascospores. This production of the *Glomerella* perithecia from sowings of conidia of *Colletotrichum* is one part of the evidence obtained in this study of the genetic connection between the two.

Inoculation Experiments.

Healthy leaves, detached as well as on cut shoots of *Tinospora cordifolia,* were inoculated on the lower surface with *Colletotrichum* spores. The detached leaves were incubated in a damp chamber and the inoculated shoots were covered with bell jars. All the glassware used in this connection had been carefully washed with 3% Lysol solution. Controls were kept.

Signs of infection were first seen on the fourth day, generally, at the points of inoculation. The infection extended fairly rapidly and on the sixth or seventh day the leaves were completely discoloured. On the tenth or eleventh day, minute black bodies were noticed which turned out to be *Colletotrichum* acervuli in which setæ were invariably present. After nearly a week more, bigger and more prominent black bodies developed which were the perithecia of *Glomerella,* producing asci and ascospores. (Fig. 5). The controls remained healthy in all cases.

In all, 57 inoculations were made and all but 6 were successful. These results place beyond doubt the parasitic nature of the *Colletotrichum* on *Tinospora cordifolia.*

Development in Moist Chambers.

In the months of August, September and December 1930, leaves with *Colletotrichum* on them were washed with corrosive sublimate (1 in 1000) to destroy the spores of any foreign fungus if present on

the surface and then thoroughly rinsed with sterile water. These were afterwards incubated in a damp chamber. After 12-14 days these leaves developed the characteristic perithecia of *Glomerella* with asci and ascospores. In measurements these agreed with similar structures obtained both in nature and in the cultures.

(ii) *The Glomerella Stage.*

This was found in the mature stage only on leaves which had overwintered in nature. Dry, fallen leaves collected in the months of April and May show the perithecia in abundance. They are formed singly or in clusters, are flask-shaped and beaked bodies, opening by a distinct mouth and measuring 90-140μ in diameter, (Fig. 6). The asci are clavate, sessile and measure 44-67μ by 7-12μ. Each ascus contains eight spores arranged roughly in two rows. (Fig. 7). The ascopores are more or less curved, unseptate and with rounded ends, hyaline and measure 13-19 μ by 4-7 μ. (Fig. 8).

From these characters the perithecia could be easily identified with those of *Glomerella cingulata* (Ston.) S. & v. Sch.

Growth in Pure Cultures.

The ascospores germinate readily in water. Within a period of 20-21 hours a germ tube is protruded from one end of the spore and this develops into a long septate hypha which is narrow, hyaline and granular and vacuolate. Oil droplets are also present in it. An appressorium is formed at the end of this hypha after it has grown to some length. (Fig. 9).

Sowings of single ascospores on glucose-peptone agar give on the second day a white mycelial growth which soon turns pink. It consists of numerous, narrow as well as broad, freely branching hyphæ which are closely septate and vacuolate. On the fourth day, usually, conspicuous, black dots are developed in the cultures which under the microscope are seen to be acervuli of *Colletotrichum* with characteristic setæ and spores. On about the eleventh day from the start of the cultures other black bodies different from the *Collectotrichum* acervuli appear which are easily made out to be the perithecia of *Glomerella.* These agree in all respects with similar bodies found on leaves in nature and those developed in the inoculation experiments and in moist chambers.

The production of the *Colletotrichum* stage from sowing of the ascospores in these cultural studies furnishes the second part of the evidence of the genetic connection between the *Glomerella* and *Colletotrichum* stages which is thus completely proved.

Inoculation Experiments.

Healthy leaves, detached as well as on cut branches of the host,

were inoculated on their lower surfaces with ascospores and kept in damp chambers or under bell jars. Controls were kept in all cases.

On the third or fourth day, signs of infection were observed in the inoculated places in the form of small discoloured patches. These gradually increased in size until, on the seventh or eighth day, small, black dots appeared on them. These, on microscopic examination, were seen to be *Colletotrichum* acervuli with the characteristic, dark brown setæ. These were followed after a week by bigger black dots which were made out to be perithecia of *Glomerella,* with asci and ascospores. The controls remained healthy in all cases.

In all, 40 inoculations were made and all gave positive results except two. The *Colletotrichum* stage was thus produced from *Glomerella* ascospores in these inoculation experiments as the *Glomerella* stage had been previously obtained in the inoculations with *Colletotrichum* conidia. Thus the results of the inoculations confirm those of the cultural studies.

Discussion.

In this study the conidial form (*Colletotrichum*) and the ascigerous form (*Glomerella*) occurring on *Tinospora cordifolia* have been proved beyond doubt to be genetically connected. Not only have the perithecia been found to succeed regularly the *Colletotrichum* stage in nature but the two stages have been reproduced from each other in cultures both on natural and artificial media. This adds one more to the number of cases in which this genetic connection between these two spore forms has been proved by previous workers.

The parasitism and pathogenic nature of both the *Colletotrichum* and the *Glomerella* stages on *Tinospora* have also been proved beyond doubt by the inoculation experiments. Although in nature the perithecia have been found to occur chiefly on dead and decaying leaves, the ascospores have been shown easily to cause infection of healthy leaves. This experience is opposed to the suggestion made by Appel and Wollenweber (according to Shear and Wood (6)) that "the fact that an organism will complete its life history on artificial culture media or dead organic matter is an indication that it is a saprophyte." Shear and Wood (6) themselves have pointed out that this suggestion does not seem to be in accordance with the known facts. The writers' work with the *Glomerella* on *Tinospora* affords additional strength to Shear and Wood's opinion, for the fungus, though easily cultivable on artificial media, was found in this work to be fairly virulent as a parasite.

There is some indirect evidence obtained during this study that, contrary to the finding of Edgerton (4) and in agreement with the

views of Shear and Wood (6), there is probably no sexual process involved in the formation of the perithecia of *Glomerella*. The fact that the perithecial stage was developed in single-spore cultures from *Colletotrichum* would seem opposed to the theory that some kind of sexual union is necessary for the production of perithecia.

Another interesting point in the results of this study of *Glomerella* is the production of fertile perithecia on one medium (glucose-peptone agar) only of a number of others tried. This inclines the writers to believe that the production of perithecia may be, after all, a matter of the medium used, though Dastur (3) and Small (7) do not regard it so.

Finally, mention must be made of the considerable amount of infection by *Glomerella* which takes place in natural conditions in the field. Not only ordinary healthy leaves but also apparently healthy leaves which had been washed with a disinfectant to kill surface organisms frequently developed *Colletotrichum* acervuli on incubation in moist chambers. This points to the capacity of the fungus to remain uninjured by superficial treatment of the leaves with fungicides. If, as seems probable from the work of others (e. g. of Rand (5)) the numerous other *Colletotricha* which occur as parasites of cultivated plants behave similarly and remain inside even apparently healthy parts of the host and are unaffected by fungicide, they must offer problems of particular difficulty for plant pathologists to deal with practically.

Summary of Conclusions.

1. *Glomerella cingulata* (Ston.) S. & v. Sch. with its associated *Colletotrichum* occurs as a parasite on leaves of *Tinospora cordifolia*.

2. The two forms of fungi have again been proved to be genetically connected and the parasitism of both has been proved by cultural studies and inoculation experiments.

3. The perithecial stage of *Glomerella* was easily produced in single-spore cultures from *Colletotrichum* on one medium (glucose-peptone agar) only of a number of others tried. This points to the production of perithecia being a matter of the medium of growth.

4. The production of perithecia in single-spore cultures seems opposed to the theory put forward by Edgerton that some kind of sexual union is necessary for the production of perithecia in *Glomerella*.

5. The *Glomerella* here studied, though easily cultivable on artificial media, is fairly virulent as a parasite. This observation is opposed to the suggestion of Appel Wollenweber that "the fact

that an organism will complete its life history on artificial culture media is an indication that it is a saprophyte."

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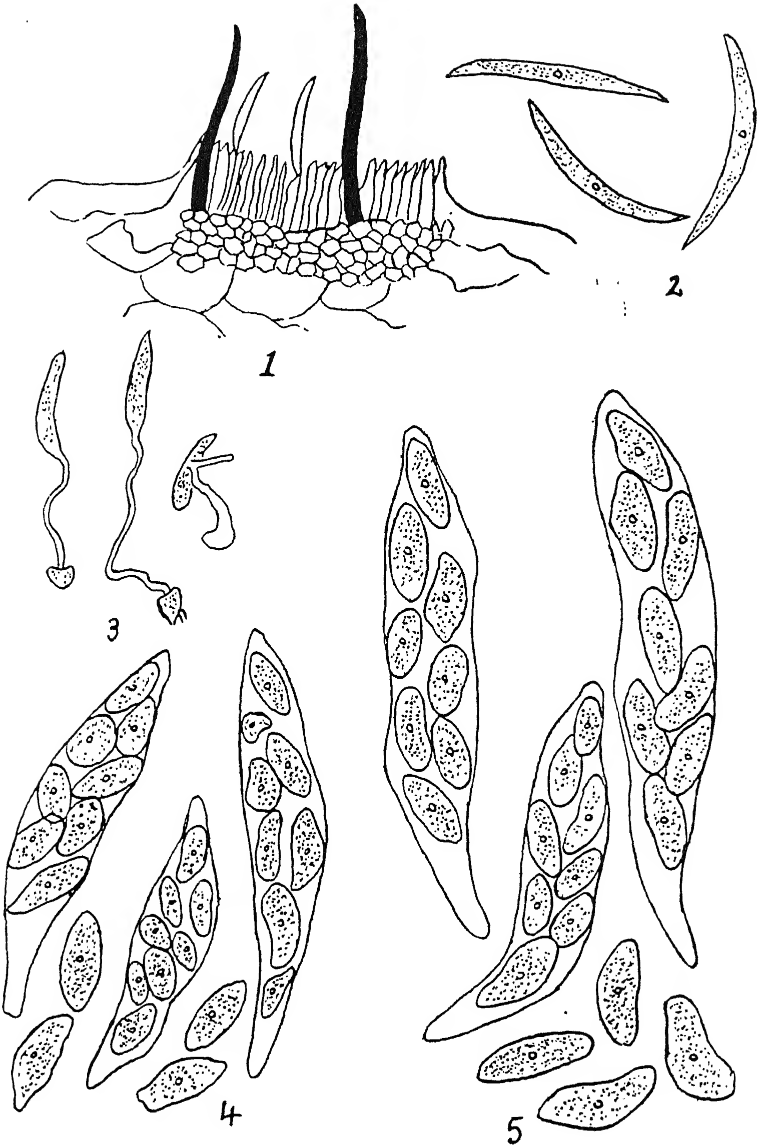

Fig. 1. Section through a Colletotrichum acervulus on Tinospora leaf. X 123.

Fig. 2. Colletotrichum conidia on Tinospora leaf. X 840.

Fig. 3. Colletotrichum conidia geminating X 123.

Fig. 4. Asci and ascospores of Glomerella from cultures. X 840.

Fig. 5. Asci and ascospores of Glomerella from a leaf from a successful inoculation expt. with Colletotrichum X 840.

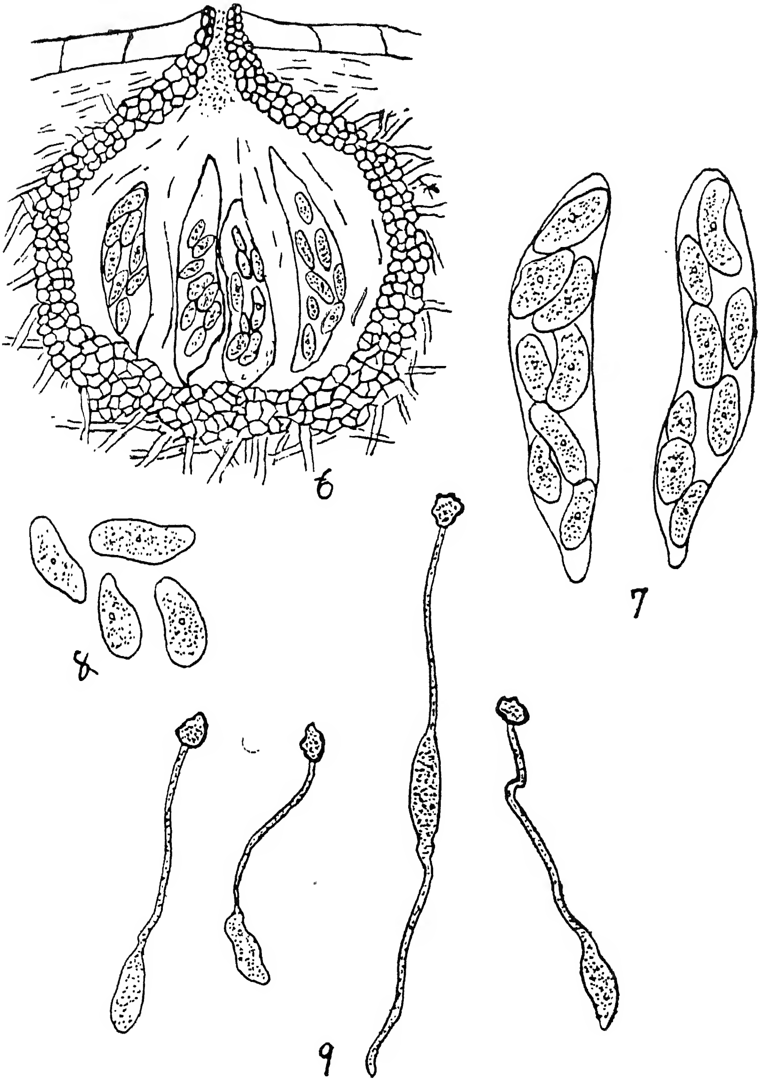

Fig. 6. Perithecium of Glomerella in section. X 420.
Fig. 7. Asci from the host in nature. X 840.
Fig. 8. Ascospores from the host in nature. X 840.
Fig. 9. Ascospores from the host in nature germinating. X. 123.

A STUDY OF *CERCOSPORA TINOSPORAE* SYD. AND ITS ASSOCIATED PYCNIDIAL AND PERITHECIAL STAGES

(With three plates)

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In our paper on *Glomerella cingulata* on *Tinospora cordifolia* which is published separately in this issue of the Journal of the Bombay University, we referred to *Cercospora Tinosporæ* with an associated pycnidial stage (*Phoma*) as occurring side by side with the *Glomerella* on leaves of *Tinospora cordifolia* and causing a leaf-spot disease. During the course of further work with the *Cercospora*, another perithecial form, distinct from the *Glomerella* was noticed and was identified with *Mycosphærella*. *Mycosphærella* has been mentioned as the perfect stage of *Cercospora* by many workers but the genetic connection between the two has been, in most cases, inferred from strong circumstantial evidence rather than proved by cultural production of the two forms, one from the other. It was, therefore, decided to see if cultural evidence of this connection could be obtained in the present case.

This paper gives an account of our studies on *Cercospora Tinosporæ* Syd. and the *Phoma* and *Mycosphærella* forms found associated with it on leaves of *Tinospora cordifolia* Miers. at Ahmedabad in North Gujarat.

PREVIOUS WORK

Cercospora Tinosporæ has been previously collected on leaves of *Tinospora reticulata* from the Phillippine Islands and was named and described by Sydow (14) in 1916. But beyond this naming and description there is no record of any previous work on this fungus. The same is true of the pycnidial and perithecial forms associated with it. These have not been previously observed or studied on *Tinospora cordifolia*.

SYMPTOMS OF TINOSPORA-LEAF-SPOT DISEASE

The disease is usually noticed on the leaves of *Tinospora cordifolia* growing wild on hedges at Ahmedabad in the month of August every year and attacks the plant very severely. It is evident in the form of numerous powdery white spots on the under surface of the leaves. The spots are angular, squarish or somewhat irregularly elongated in the direction of the long axis of the leaf. They vary in size from 0·5 mms. to 6-7 mm. In the beginning, the spots are few and scattered but later on they increase in numbers and coalescence of neighbouring spots takes place, the whole surface of the leaf being ultimately covered by them. (Photo 1.).

The colour of the spots on the upper surface of the affected leaves is bright yellow in the early stages but it fades later and in dry fallen leaves becomes a chocolate colour. The drying up of the leaves seems to be hastened by the disease.

Tinospora cordifolia retains its foliage only from July to December, *i.e.*, for a period of about six months. Spotted leaves are only found, therefore, during these months. From December onwards, the leaves begin to fall and, within a month or so, practically all the leaves are shed, usually. Young growing branches occur here and there, but the number of leaves is small and they are free from the disease. In the months of January and February the *Tinospora* flowers and produces fruits.

CERCOSPORA TINOSPORAE SYD. (THE CAUSE OF LEAF-SPOT)

The pathogen responsible for the white disease spots mentioned above is *Cercospora Tinospoæ* Syd., one of the Hyphomycetous fungi. It sporulates abundantly by the formation of conidiophores and conidia on mature lesions. It is the conidiophores and conidia which give the powdery appearance to the disease spots. The mycelium of the parasite is located in the tissue of the leaf. The young mycelium consists of septate hyphæ which ramify between the cells of the host and is hyaline in colour.

The conidiophores occur in dense aggregates and are found only on the under surface of the leaves. They are hyaline and measure 54-98μ by 4-6μ. They are closely crowded at the base of each tuft and are freely separated at the apex. The conidiophores composing a fascicle vary in number from five to as many as thirteen. There is an accumulation of stromatic tissue of a dark brown colour in the air-spaces below the stromata. This is the only part of the fungus which is coloured at this stage. The conidiophores originate from the stromata and come out through the stromatal pores. (Fig. 1). The part of the stroma bearing the conidiophores appears as a black,

conical protrusion through the stoma. When the conidiophores are removed artificially, or owing to age, these stromatic protrusions appear as black dots on the spots and may easily be mistaken on superficial examination for some kind of pycnidial bodies. But they contain no spores and are much smaller than the pycnidia associated with this *Cercospora* to be described later.

The conidiophores are generally 1-3 septate. A few of them are straight but many appear to be knotted or angled. At each angle there is a prominent scar. When a spore falls away, a scar is generally left at its place of attachment. As many as five scars have been observed on a single conidiophore, the usual number varying from 1-3. (Fig. 2.).

The conidia are attached by their broader ends. They are hyaline and usually multiseptate. They are long, narrow, rounded at the base but tapering at the apex. The apex is usually about half as thick as the base. The septa vary in number from 0 to 3. The three-septate conidia are the most numerous. The conidia measure 35-55μ by 4-7μ. (Fig. 3.).

The conidia germinate readily in water within 14-18 hours. (Fig. 4.). At first a small germ-tube protrudes from one end of the spore and this gradually develops into a long, unseptate hypha. Germ-tubes are observed to arise from the broader as well as the narrower, drawn out end. In some cases, they arise from both the ends simultaneously. They also arise from the side of the spore at an angle with its long axis. In the case of a multi-septate spore, the germ-tube may arise from any of the cells. As many as three germ-tubes have been observed developing from a single spore, but, usually, there are not more than two. In the case of slightly curved spores, a germ-tube may arise from the convex as well as the concave side. The germ tubes soon branch and, by further growth, form a septate colourless mycelium in artificial cultures.

Conidia collected on the 1st of August, 1930, and kept in the herbarium did not germinate on the 27th of October, 1930, and later. Further, conidia collected on the 27th of August, 1931, did not germinate on the 20th of October 1931. These trials go to prove that conidia on leaves kept in the herbarium lose their viability and are incapable of germination after about two or three months.

CULTURAL STUDIES WITH CERCOSPORA TINOSPORAE

Cultures were made on various nutrient media, such as, Thaxter's hard potato agar, corn-meal agar, Tinospora-plant-juice agar, glucose-peptone agar, glucose-meat-extract agar and sterilised Tinospora stem bits and on potato plugs. These media were prepared in the usual

manner and, in the case of the plant-juice agar, juice was squeezed out of the fresh healthy leaves and stems and the necessary proportion of agar-agar added to it.

The conidia germinate readily in nutrient media within a period of 12-14 hours. Growth is very slow and remains submerged for the first two days. On the third day, a superficial growth is visible to the naked eye in the form of a white, fluffy, cotton-like mass which, later, gradually develops a pink colour. The mycelium consists of thick as well as thin hyphæ measuring 2-6μ in breadth and branching freely. The protoplasm is granular and contains small oil globules. Conidia were not noticed in any of the cultures on the media used except in one solitary case on Thaxter's hard potato agar. In this case the conidia were noticed in an observation made when the culture was just 72 hours old.

Further development is marked by the appearance of small brownish bodies in the centre of the culture on the fourth or fifth day. On close examination it is observed that the hyphæ gather at some places in the culture and form stroma-like masses from which these brownish bodies are developed. They are spherical or oval in shape. A circular mouth is distinctly seen at the apex in the majority of these bodies, although those with two mouths are not uncommon. The wall of these bodies is made up of pseudoparenchyma and as they contain a mass of spores held in a gelatinous matrix which comes out through the mouth in a worm-like manner, they can be recognised as pycnidial bodies. Sometimes two or three pycnidia are attached together. Mycelial growth in the cultures is scanty as compared with the copious growth of the pycnidial bodies which are developed in more or less concentric rings. From the characteristic mode of ejaculation of spores these pycnidial bodies were referred to the Genus *Phoma*. Observations were continued but no further development was noticed.

Sub-cultures were started from the mycelium resulting from the sowing of *Cercospora* conidia on Thaxter's potato agar, Tinospora-plant-juice agar and corn-meal agar. In these at first a submerged growth was observed which became more evident later as a white fluffy superficial growth. A pink colour was gradually developed which was more marked at the part of the medium in contact with the glass. This was followed on the 4th or 5th day by the development of pycnidial bodies. The mycelial characters were the same as before. The cultures were kept for fourteen weeks but no further development was noticed.

Many repetitions of such cultures invariably gave the same sequence of results.

Another series of cultures was made from pycnospores obtained from the sowing of *Cercospora* conidia on various media mentioned above. There was invariably a white fluffy growth observed first and this was immediately followed by the development of the pycnidial bodies. The mycelial characters were the same as in the cultures from *Cercospora* conidia and even cultures kept for fourteen weeks showed no further development. Numerous repetitions of these cultures gave the same results. No higher form, nor even the original *Cercospora* form, was obtained in any of the cultures.

It was thus found that the growths obtained from the sowings of *Cercospora* conidia and of pycnospores resulting from them were identical.

In order to confirm the production of pycnidia from the sowings of *Cercospora* conidia, a large number of fresh isolations were made by various methods and on various nutrient media, including partially sterilised *Tinospora* stem bits but the results were in every case identical with those mentioned above.

INOCULATION TRIALS WITH CERCOSPORA

A large number of seedlings were raised in pots for inoculation experiments during the rainy seasons of 1931 and 1932 and, every time, most of the leaves developed, within a few days, the characteristic *Cercospora* spots like those observed in nature. This was remarkable as the seeds, before sowing, had been, in every case, washed with corrosive sublimate solution (1 in 1,000) and rinsed thoroughly with distilled water afterwards. The appearance of the disease in spite of these precautions suggested that the seeds harboured the fungus in some way and thus acted as carriers of infection. It was thus found impossible to carry out the inoculation experiments on plants raised in pots from seed. The inoculation experiments, therefore, had to be carried out with healthy leaves and branches of the host plant cut under water. Controls were kept in all cases.

53 inoculation experiments were made in all which gave mostly negative results. In some cases there were slight indications of infection but no spores were formed. Two positive results, however, were obtained and these leave no doubt as to the causal connection of the fungus with the disease. The following are the details of the successful inoculation experiments :—

On 5-9-31, five healthy branches were cut under water and kept in five separate cylindrical glass jars provided with covers and washed previously with 3% Lysol solution. One leaf of each branch was inoculated on the lower surface only with fresh *Cercospora* conidia by placing a drop of a suspension of conidia in sterilised water,

The jars were then covered. Two controls were kept alongside.

On 10-9-31, the inoculated leaves showed signs of infection at the place of the inoculum and the infected areas had become pale. The spots gradually increased in size and on 15-9-31, characteristic *Cercospora* spots were developed. White clusters of conidiophores began to come out and these produced the *Cercospora* conidia. In appearance the spots were exactly similar to those in nature. (Photo. 2). Scraping the white spots exposed small, black stromatic points. On the upper surface of the leaf in the infected spots a yellow colour was developed. On 20-9-31, all the five infected leaves were detached from the branches and placed in a damp chamber to observe further development. On 27-9-21 small, dark bodies were observed in close association with the *Cercospora* spots. On microscopic examination they were found to be pycnidia of *Phoma*. In hand sections it was observed that the *Cercospora* mycelium had developed these pycnidial bodies. They had a distinct mouth through which the spores came out in the characteristic worm-like manner. The *Cercospora* was re-isolated from the successfully inoculated leaf on Thaxter's hard potato agar.

On 29-9-31, two healthy detached leaves were inoculated on the lower surface with a little mycelium from the above re-isolation and then placed in a moist chamber previously disinfected with 3% Lysol solution. A control was kept.

On 5-10-31, signs of infection were observed at the points of inoculation but no fructification was noticed. The spots gradually increased in size and on 20-10-31, small black bodies appeared in the inoculated places. These were the pycnidial bodies associated with *Cercospora*. No *Cercospora* conidia, however, were seen.

The controls in the case of both these experiments remained healthy.

PENETRATION OF THE HOST BY CERCOSPORA

Hand sections of some of the inoculated leaves were taken every twenty-four hours after inoculation in order to observe the penetration of the fungus. The germ-tube was observed in one case distinctly to have penetrated the epidermal wall directly (Fig. 5). Hyphae were also seen in the epidermal cells. In no case was a germ-tube observed to pass in through a stroma.

DEVELOPMENT OF CERCOSPORA IN MOIST CHAMBER

In order to follow the progress of the *Cercospora* on the fallen leaves to see if any other stages were developed, during the month of August, when the disease made its appearance, of the years 1931

and 1932, fresh spotted leaves were brought from the field and kept in damp chambers which had been thoroughly disinfected previously with Lysol solution. At the time of collection the leaves only showed the *Cercospora* spots. Day to day observations were made and it was found that after a week, small, brown or black spherical bodies were visible in association with the *Cercospora* spots. On microscopic examination it was observed that these bodies were developed on a mass of hyphæ forming a stromatic tissue and were surrounded by similar hyphæ. Observations were continued for several weeks but no further development took place. It appeared as if these bodies were either incipient pycnidia or perithecia, similar to those found on the leaves of the host while still on the plant. Even in nature, mature pycnidia are found only on fallen leaves. In four cases in these observations on leaves in moist chamber mature pycnidia were seen to have developed. But with regard to the development of perithecia, the results were entirely negative.

PHOMA STAGE ON TINOSPORA CORDIFOLIA

Dry fallen leaves collected in the month of December and later showed minute dark brown bodies in close association with the *Cercospora* spots. These were evidently the mature stages of the spherical bodies collected earlier and referred to in the previous paragraph. These had a distinct circular mouth and contained a mass of hyaline, one-celled spores, held together by a gelatinous substance which exuded through the mouth in a worm-like manner.

These pycnidia are developed on the mycelium which traverses the tissue of the leaf underneath the epidermis (Fig. 6). They measure 40-120μ in diameter. Conidiophores are absent. The spores are uni-cellular, hyaline, cylindrical or rod-shaped. They measure 4-7 μ by 3-4 μ. Pycnidia obtained in culture from the sowing of *Cercospora* conidia measure 35-118μ in diameter and the spores measure 4-7μ by 3-4μ, so that it can be said that the pycnidia associated with the *Cercospora* in nature and those obtained in cultures from sowings of *Cercospora* spores have practically the same measurements.

A large number of germination trials in distilled water and various nutrient media were made with the pycnospores obtained from the host in nature but they were uniformly unsuccessful. The pycnospores formed in cultures, however, did germinate (Fig. 7) and the possibility of their still being functional is not to be lost sight of.

Pure cultures from sowings of pycnospores obtained in cultures have already been described under *Cercospora*. (P. 69).

Inoculation experiments were carried out on healthy, detached leaves with pycnospores formed in nature as well as in cultures and with mycelium obtained from pycnospores. The results were negative in all cases.

MYCOSPHÆRELLA STAGE

Over-wintered leaves collected in the months of April, May and later show large, black bodies in the tissues killed by *Cercospora Tinosporae* in close association with it. These were made out under the microscope to be distinct perithecial bodies having the characters of *Mycosphaerella.*

These perithecia are formed on, or somewhat immersed in, a stroma formed of interwoven hyphae in the tissues of spotted leaves. They are more or less ovate, black in colour, with a brownish wall composed of one or two layers of pseudoparenchyma (Fig. 8). They measure 59-68 μ by 66-95 μ in diameter. They contain club-shaped asci with eight spores (Fig. 9). Paraphyses are absent. The spores are bi-seriate, elliptical, uni-septate, hyaline and measure 14-16μ by 3-4 μ in diameter.

The ascospores germinate readily in water and nutrient media. (Fig 10). A short germ-tube is protruded from one end of the spore and this develops into a long septate hypha which is hyaline and has granular contents.

Cultures made on corn-meal agar gave at first a white mycelial growth which soon became pink in colour. All the cultures remained sterile although kept for over two months. Repeated trials gave the same result.

The cultural characteristics of the sterile mycelium obtained from sowings of the ascospores were, however, quite similar to those of the first sterile pink mycelial growth obtained from the sowings of *Cercospora* conidia on the same nutrient medium.

All attempts to infect *Tinospora* leaves in the laboratory by means of ascospores have been unsuccessful.

DISCUSSION

In the field and cultural studies of *Cerospora Tinosporae* Syd. and the *Phoma* and *Mycosphaerella* forms found associated with it recorded above, a clear indication has been, once again, obtained of the genetic connection between the three.

The pycnidial bodies succeed the *Cercospora* in close association both in nature and in artificial cultures. The pycnidia have been obtained invariably from sowings of *Cercospora* conidia, not only on agar slants but also in hanging-drop cultures where the possibility

of overlooking any contamination was precluded. This production of pycnidial bodies in cultures from sowings of *Cercospora* conidia is paralleled in the works of others, notably Jenkins, (7) Higgins, (4,5) Demaree and Cole, (3). The measurements of the pycnidia and pycnospores in nature and cultures agree. The only difference is that pycnospores from cultures germinate, while those from pycnidia from fallen leaves in nature failed to do so.

The proof of the genetic connection between the *Cercospora* conidial stage and the ascigerous *Mycosphaerella* stage is less complete, as no actual *Cercospora* conidia were produced in our cultures from sowings of the ascospores of the *Mycosphaerella.* The mycelium resulting from such sowings remained invariably sterile, but it showed strong resemblances to the mycelium resulting from the sowings of *Cercospora* conidia and of pycnospores obtained in our cultures and this may be regarded as making the genetic connection between the three forms at least highly probable.

Sowings of *Cercospora* conidia failed to reproduce the conidial stage in all the cultures on all the media tried except once on Thaxter's potato agar, and, though the pycnospores obtained from *Cerospora* conidia did germinate, they failed to reproduce any other stage of the fungus but invariably gave rise to pycnidia.

It is interesting, in this connection, to recall that O'Gara (9) reports that "the examination of many specimens (of Asclepias) showed that in every instance it (*Phoma*) was associated with *Cercospora clavata* (Gir) Peck. The leaf and stem spots always showed the presence of both *Phoma* and *Cercospora clavata* (Gir) Peck. Often the pycnidia of *Phoma* and the acervuli of *Cercospora* were intermingled." Also Wolf, (15) working with the Pomegranate Blotch caused by *Cercospora lythracerum* in Florida, found that "a spermogonial stage occurs during autumn on the lower surface of lesions caused by the *Cercospora* stage" which, he thought, was strong circumstantial evidence to regard it as a stage in the life-history of the *Cercospora,* though he was not able to obtain actual cultural evidence for it. In describing this stage of the Pomegranate *Cercospora* Wolf further says that it was "pycnidial in structure" but he regards the fact that all efforts to germinate the pycnospores produced from the pycnidial bodies failed as evidence that "they are not conidia of a saprophytic species of *Phyllosticta* but are homologous with what have been termed spermatia." All the other workers on *Cercospora* whose published papers we have been able to have access to (Jenkins, (7) Higgins, (4, 5) Demaree and Cole, (3) Latham (8) etc.) record a similar experience with the pycnospores associated with *Cercospora.* These have in-

variably failed to germinate. The fact that pycnospores formed *in nature* on *Tinospora* leaves have also failed to germinate indicates a similarity between the pycnidial bodies of the *Cercosporas* occurring on such a variety of hosts as, Pomegranate, Tinospora, Cherry, Cowpea, Pecans, Grapes, etc.

The genetic connection between the conidial *Cercospora* and the ascigerous *Mycosphaerella* has been shown to be more than probable from the evidence obtained in the work of the authors mentioned already. The occurrence of the *Cercospora* with its associated pycnidial stage and the *Mycosphaerella* in sequence in the same lesions on one host, the production of pycnidia from sowings of *Cercospora* conidia in artificial cultures and the similarity of cultures from conidia and ascospores have been noted by all these workers and are confirmed by our own experience with *Cercospora Tinosporae.* But convincing cultural proof of the genetic connection was furnished, so far as we know, only by Jenkins (7) and by Latham (8).

Jenkins working with *Cercospora cerasella* Aderh. and, very recently, Latham working with *Cercospora cruenta* Sacc. on Cowpea, were able to obtain *Cercospora* conidia in cultures starting from ascospores. But even these authors have not succeeded in getting perithecia from sowings of Cercospora conidia. Our experience with the *Cercospora Tinosporae* has been the same. Although we were fortunate in getting the pycnospores obtained in our cultures to germinate (no previous worker, so far as we know, has been able to germinate the pycnospores, whether obtained in nature or culture) the growth from pycnospores consisted invariably of pycnidia again and we have had no better luck than others with regard to the development of perithecia in cultures.

The non-production of *Cercospora* conidia in most of the artificial cultures on various media is a striking experience in this study but this also is paralleled in the work of Wolf above mentioned as well as in that of Rend (12) working with the Brown leaf-spot of Pecan and that of Singh (13) in his studies in the genus *Cercospora.* Wolf states that "all cultures both from ascospores and from conidia have remained sterile", while Rend reports that no distinct development of *Cercospora* conidia was observed by him in cultures of the fungus. Singh also found that, of the four species of *Cercospora* he studied at Allahabad, one, *C. Feuilleauboissi* Sacc. "failed to form conidia on any of the media tried. Even six months old cultures of this species did not show conidia." Singh, however, mentions chlamydospores being formed in abundance in this as well as other *Cercosporas* studied by him. The writers have not noticed any such in their cultures.

Latham (8) suggests an explanation of this apparent sterility of cultures of *Cercospora*. He found in his studies with *Cercospora cruenta* Sacc. that he had to examine very young cultures to be able to find conidia in them. Conidia, he found, began to appear after about 36 hours from the starting of the cultures and were rather numerous after about 48 to 72 hours. He states, further, that conidia were scarcely ever found in cultures over five days old. The fact that in the solitary instance in our experience when we obtained conidia in our cultures from sowings of *Cercospora* the culture happened to be examined when it was 72 hours old, seems to corroborate Latham's observation. Cultures of *Cercospora* are generally inconspicuous for the first two days and pycnidia begin to form almost immediately afterwards and, as Latham has found, no conidial formation takes place in older cultures. This explains probably, how we missed the conidial formation in most of our cultures.

The comparative failure of the inoculation experiments with *Cercospora Tinosporae* which is another notable point in this study impresses one with the imperfection of our knowledge of the conditions influencing successful infection by fungi. The majority of the *Cerocospora* inoculations failed, though at least two of them were convincingly successful. No explanation can be given of either the failure or the success, nor is there any light available on this point from the work of others. Similar failure in securing artificial infection of sugar-beet plants in Colorado led to two very exhaustive studies by Pool and McKay (10, 11) on the relation of stomatal movement and climatic conditions to infection by *Cercospora beticola* causing leaf-spot disease of Sugar-beet. These authors have found a definite relationship between stomatal activity (opening and closing under the action of certain morphological and environmental factors) and infection by the Sugar-beet *Cercospora,* in which penetration of the leaf by the conidial germ-tube has been observed to occur only through open stomata. Any such relation seems, however, to be precluded in the case of *Cercospora Tinosporae,* as the penetration has been ascertained here to take place through the epidermal cell walls and not through stomata. In this mode of direct penetration *Cercospora Tinosporae* also differs from *Cercospora fusca* causing Brown leaf-spot of Pecan in which, Rend (12) thinks that the fungus in all probability enters the host through stomatal openings ; but it resembles *Cercospora cerasella* causing leaf-spot of Cherry, in which, as Jenkins (7) states, "the germ-tubes from conidia sown on the surface of the living leaves were found entering the leaves by direct penetration."

Another point that deserves special mention in the life-history

of *Cercospora Tinosporae* as revealed in this study is the indication, obtained in the attempts to raise healthy plants from seed for inoculation experiments, of the occurrence of copious seed-infection. Although great precautions were taken to disinfect the surfaces of seeds by first immersing them in 95% alcohol for a few seconds to wet the surface, then transferring them to corrosive sublimate solution (1 in 1000) and finally rinsing in sterile water, the plants raised from them frequently developed some disease spots—a phenomenon strikingly in contrast to the failure of the fungus when all the favourable conditions that could be thought of were provided for it in the inoculation experiments.

The exact manner in which the fungus perennates has not been ascertained and though, from the fact that plants raised from seeds showed the disease at a very early stage, it would seem likely, on the analogy of *Cercospora medicaginis* E. & E. studied by Hopkins (6) on Bur clover, that the seeds harbour the mycelium of the fungus, no actual proof of its existence was obtained in this work. This point, however, is important and requires further investigation. In any case it seems unlikely that the conidia can carry the *Cercospora* over from year to year. In the laboratory they have been found to lose their germinating capacity in about three months.

The total failure to germinate of pycnospores from pycnidia collected in the field suggests that this spore-form cannot be of much importance in reproducing the disease. The uniformly negative results of the inoculation experiments with pycnospores in this work point in the same direction. It is possible, however, as suggested to us by Dr. Mundkur of the Imperial Agricultural Research Institute, Pusa, in a private communication, that we have here to deal with a case of heterothallism similar to that discovered by Craigie (1, 2) in connection with the spermogonia (pycnia) of *Puccinia Helianthi* and *P. graminis*. The coming together of mycelia from pycnospores of different strains may be a necessary condition for the formation of perithecia. It has not been possible so far, to put this suggestion to experimental test.

The possibility of the sclerotia-like masses of mycelium (from which the conidiophores of *Cercospora* arise) acting as perennating bodies in the fallen leaves is indicated by Pool and McKay's (11) observation on *Cercospora beticola*.

Altogether, this study of *Cercospora Tinosporae* and its associated pycnidial and ascigerous stages reveals a number of important points in the morphology and physiology of the genus *Cercospora* which would be of interest to those who have to deal with the numerous *Cercospora* diseases of cultivated plants.

In conclusion, we wish to express our gratitude to the Director of the Imperial Agricultural Research Institute, Pusa, and the Principal, Agricultural College, Poona for loan of literature and to Dr. V. N. Likhite of Baroda and Dr. Mitra and Dr. Mundkur of Pusa, for suggestions regarding, and loan of, relevant literature. We are also much indebted to Mr. R. N. Sutaria of the Biology Department, Gujarat College, Ahmedabad, for valuable assistance in the preparation of the illustrations.

SUMMARY

1. *Cercospora Tinosporae* Syd. occurs as parasite on leaves of *Tinospora cordifolia* Miers. Associated with it there is a pycnidial form (*Phoma*) and an ascigerous form (*Mycosphaerella*).

2. This study of the *Cercospora, Phoma* and *Mycosphaerella* occurring together on one host gives a clear indication of their genetic connection and confirms the observations of other workers with these forms.

3. The pycnidial form is produced readily in artificial cultures from sowings of the *Cercospora* conidia.

4. The pycnidial stage found in nature abundantly along with the *Cercospora* is very similar to that obtained in cultures. The pycnospores formed in nature, however, have failed to germinate in the laboratory, while those from cultures germinated readily.

5. The ascigerous stage, though found in nature, has not been obtained in cultures.

6. The parasitism of *Cercospora Tinosporae* Syd. has been proved by inoculation experiments.

7. The penetration of *Cercospora Tinosporae* Syd. takes place by the hyphae boring through the epidermal walls of the host directly and not through stomatal pores as in the case of some other *Cercosporas.*

8. There are strong reasons to believe that seed-infection occurs in the case of *Cercospora Tinosporae.*

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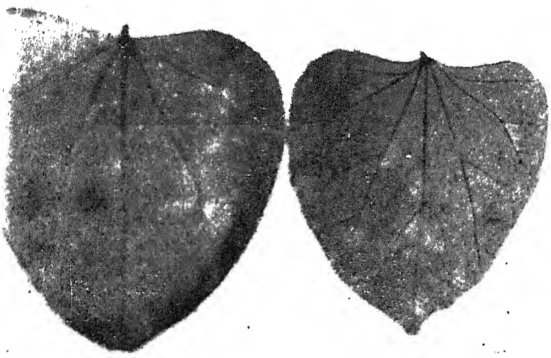


Photo. 1. *Tinospora* leaf showing white *Cercospora* spots.

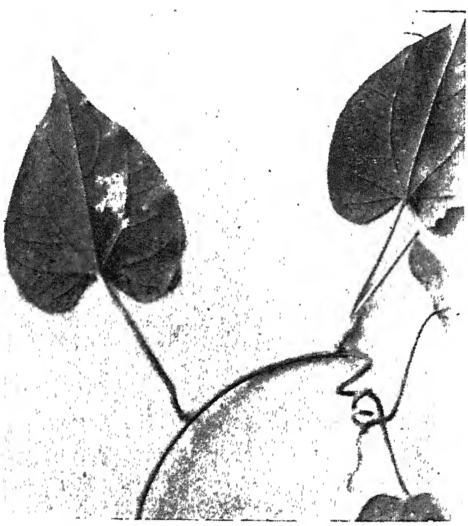


Photo. 2. *Cercospora* leaf-spot produced in Inoculation experiment.

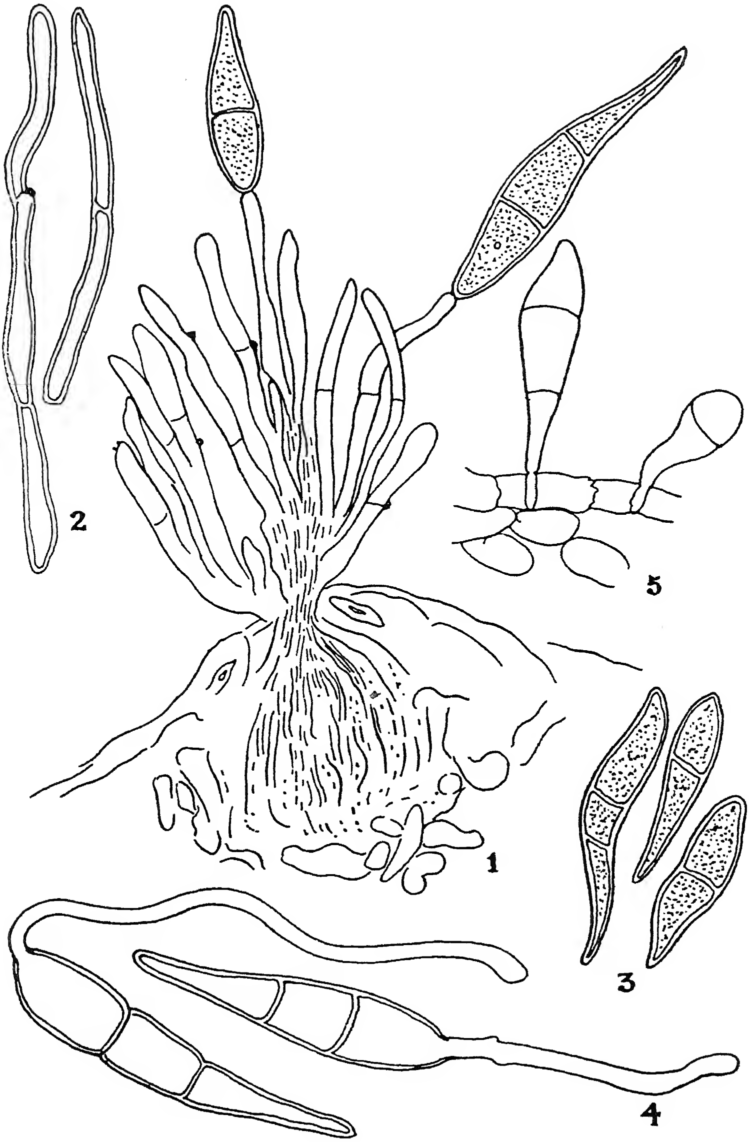


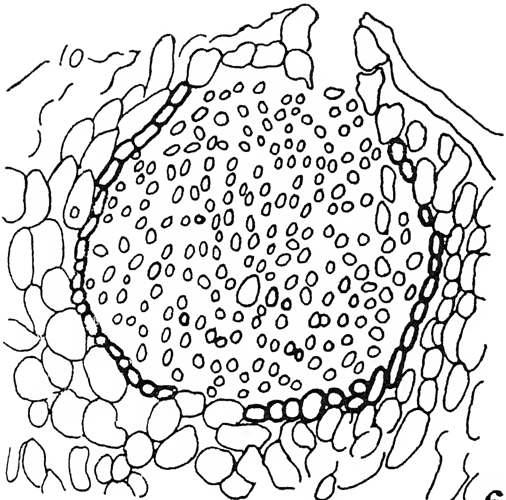
Fig. 1. Section through a stoma of leaf of *Tinospora* showing a fascicle of conidiophores of *Cercospora* and the stroma from which it arises. X 840.

Fig. 2. Separate *Cercospora* conidiophores to show scars left by conidia falling off. X 840.

Fig. 3. *Cercospora* conidia. X 840.

Fig. 4. *Cercospora* conidia. germinating. X 840.

Fig. 5. Penetration of the host by the *Cercospora* conidial germ-tube. X 840.



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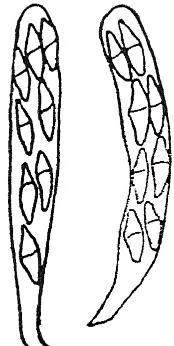

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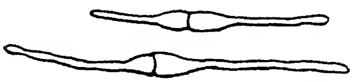

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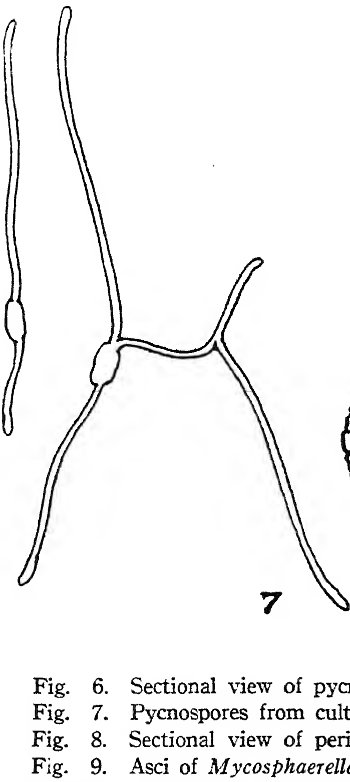

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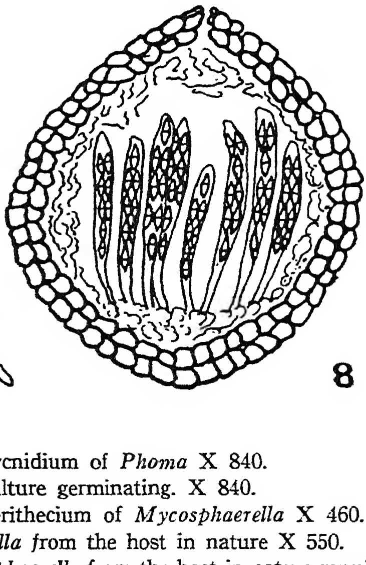

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Fig. 6. Sectional view of pycnidium of *Phoma* X 840.
Fig. 7. Pycnospores from culture germinating. X 840.
Fig. 8. Sectional view of perithecium of *Mycosphaerella* X 460.
Fig. 9. Asci of *Mycosphaerella* from the host in nature X 550.
Fig. 10. Ascospores of *Mycosphaerella* from the host in nature germinating. X 550.

CLINICAL OBSERVATIONS AND LABORATORY FINDINGS IN CASES OF ABDOMINAL TUBERCULOSIS, PARTICULARLY INTESTINAL TUBERCULOSIS, WITH SPECIAL REFERENCE TO CALCIUM CONTENTS OF THE BLOOD IN SUCH CASES.

By

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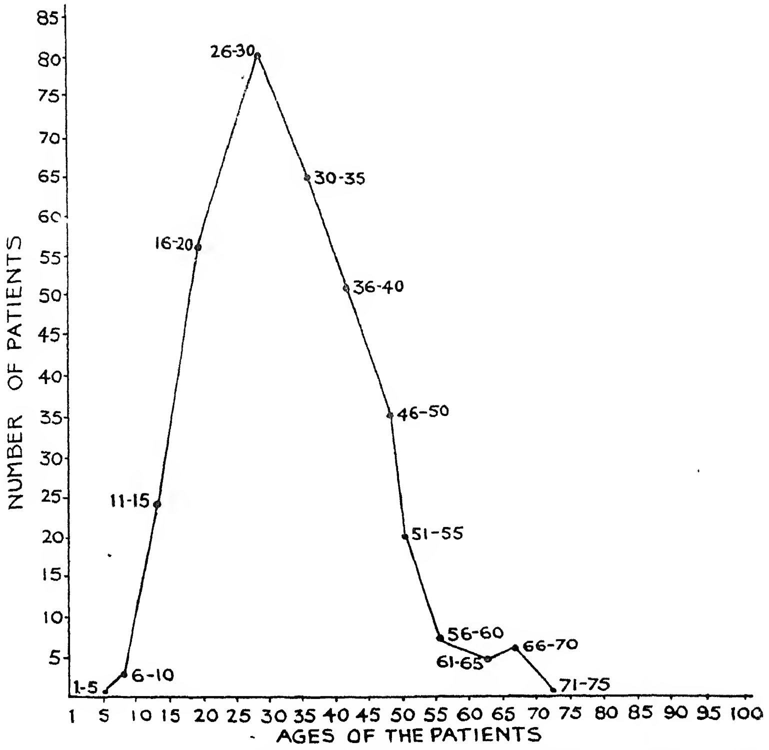
This subject of Abdominal Tuberculosis first attracted my attention when two of my friends were the victims of this disease, and when I was working as a Clinical Registrar in the Senior Medical Wards of the J. J. Hospital I was struck by the commonness of this usually unsuspected condition. Between 1922-1929, most of the observations and investigations were carried out in the wards of the J. J. Hospital and laboratories of the Grant Medical College when I was working there. The remaining cases have been picked up in private practice during subsequent years.

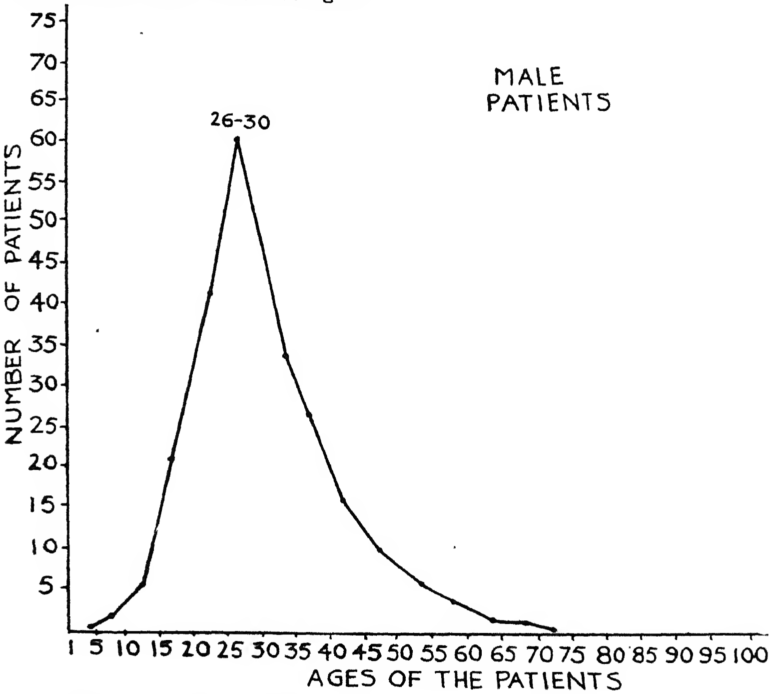
CLINICAL DATA

In all, 356 cases were investigated, out of which 235 were males and 121 females. As for age incidence there were cases of all ages ranging from 4 to 72 years, the largest percentage being between the ages of 26 and 30 years. Among the 235 male cases, the largest percentage was also between 26 to 30 years, while among the 121 female cases, the highest percentage was reached between the ages of 21 to 25, the same being maintained at the ages of 26 to 30 years. Nearly 70 per cent. or more of these cases were between the ages of 16 to 35 years. For further details refer to graphs 1, 2 and 3.

In the more advanced and severe cases, though the leading symptoms, the primary complaint and clinical evidence were of Abdominal Tuberculosis, in about 50% of these cases signs of Pulmonary



Graph 1.—Graph showing the number of patients and their ages among the 356 cases that were investigated.

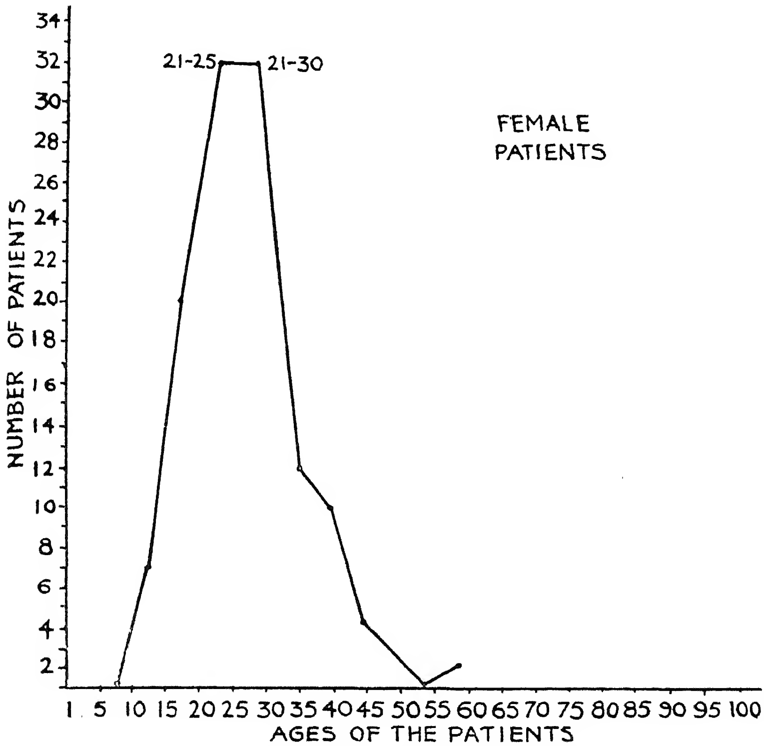


Graph 2.—Graph showing the number of patients and their ages among the 235 male cases out of the total 356 cases.

Tuberculosis were present; in about 30% there was absolutely no clinical evidence of pulmonary involvement, while in the remaining there were a few signs of Asthma or Bronchitis which by themselves were not enough to warrant the diagnosis of Pulmonary Tuberculosis

SIGNS AND SYMPTOMS

General.—In cases of Tuberculosis of Intestines, the earliest complaint may be either anorexia or indigestion, symptoms which in these cases do not generally respond in due time to the usual treat-

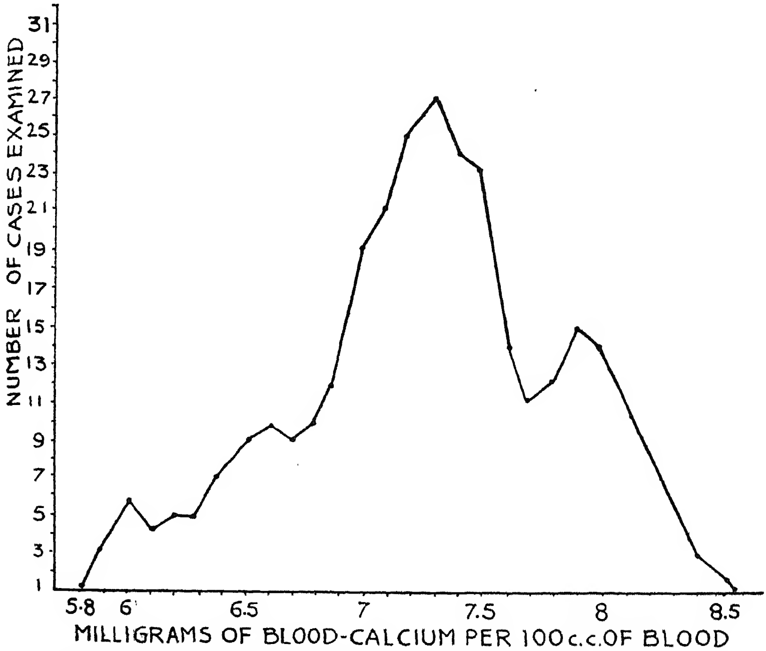


Graph 3.—Graph showing the number of patients and their ages among the 121 female cases out of the total 356 cases.

ment by diet and drugs. In most cases there is diarrhœa and in a few cases constipation, while in some, a history of diarrhœa alternating with constipation. There may be dull-aching pain in the epigastrium, which often has no relation to food, though in rare cases the pain may become worse after food. The pain might be in the right iliac fossa, sometimes simulating appendicitis and may become worse after irregularity of bowels. In such cases, on careful palpation a lump is generally felt in the area, the cæcum being palpable and tender. Often the pain is felt all over the abdomen. If only the

small intestines are affected, but for a little resistance, sometimes nothing can be made out on palpation.

Whenever the mesenteric glands are involved the patient generally complains of pain in the umbilical area, the pain being of a dull-aching or dragging character and sometimes localised. In Tabes Mesenterica constipation is far more common than diarrhœa. On palpation a lump or a resistant mass can generally be felt on one side or other of the umbilicus and on deep pressure some resistance or tenderness may be elicited. Unless the patient be very emaciated and the abdominal wall quite lax, the matting of these is difficult to be made out on palpation. In one case in a young man, one of these

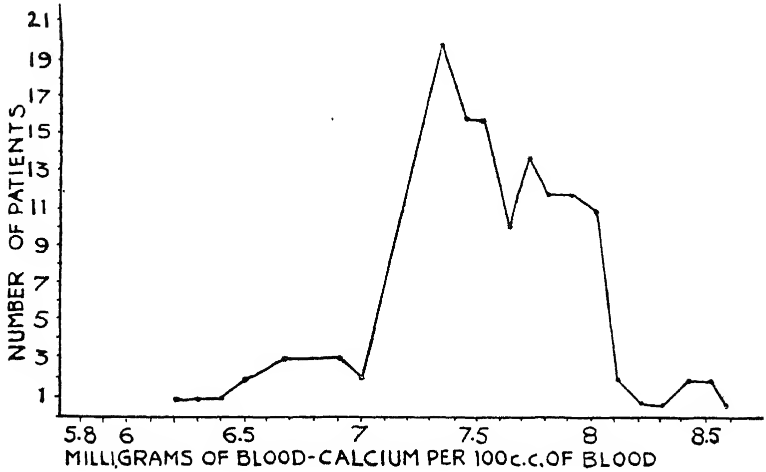


Graph 4.—Graph showing the number of cases and the amount of Calcium in blood among the 292 cases in which blood-calcium was estimated.

glands was situated in the pelvis between the neck of the bladder and the rectum which on rectal examination could have easily been mistaken for an enlarged prostate.

Whenever the peritoneum is chiefly involved the patient generally complains of pain and tenderness all over, though in exceptional cases, there may be localised areas of pain and tenderness. In dry Tubercular Peritonitis, the abdomen is sunken, tense and rigid, and irregular masses may be felt in some regions. Generally there are peritoneal adhesions. In cases of wet Tubercular Peritonitis the

abdomen is bulging with protruding umbilicus and on palpation feels soft and doughy. The quantity of fluid in the peritoneum is generally little and if it is loculated by adhesions, shifting dullness cannot be elicited. In such cases there is generally not much pain. It is most uncommon for the peritoneum alone to be affected; it generally follows the affection of some other organ in the abdomen.



Graph 5.—Graph showing the number of cases and the amount of blood-calcium among 124 cases in which Tubercle bacilli were not found either in sputum or in fæces.

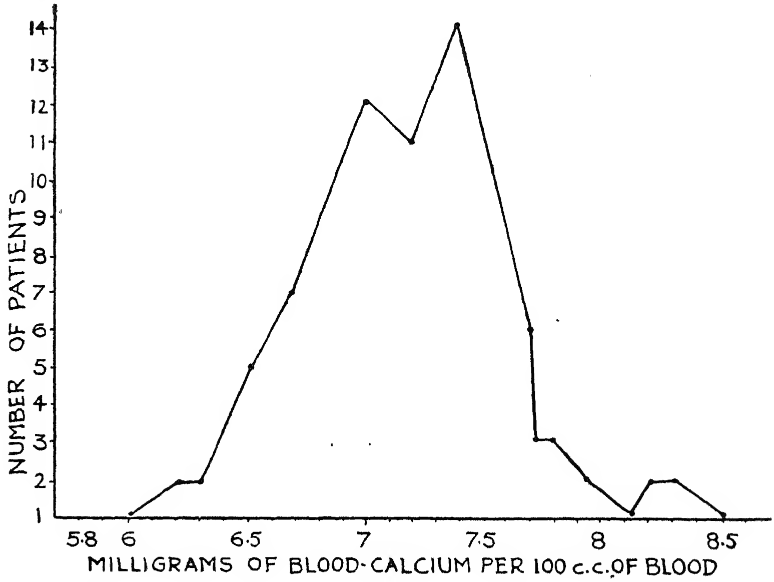
Adhesions are often formed, when the patient complains of pain referable to the particular organ involved. In one case the patient complained of pain and nausea, worse after food, sometimes relieved after vomiting but laparotomy revealed Tuberculosis of the intestines and peritoneum with many adhesions producing in some places stricture of the bowel. Whatever signs and symptoms the patient may or may not show, the most common features are—anorexia, dyspepsia, gradual loss of weight and irregular bowels, sometimes constipation, sometimes diarrhœa, sometimes both, one alternating with the other. The clinical signs do not always convey the exact idea about the severity, seriousness and extent of the lesion. It was seen in the cases in which laparotomies were performed that excision or any surgical interference was out of question in most cases, though it was considered possible on clinical examination before the abdomen was opened. The findings at the autopsies of the 35 cases also confirm the same.

In some cases, particularly those in which the patients had diarrhœa, the tongue was raw and red, denuded of epithelium simulating the so-called 'Sprue tongue'. In cases of diarrhœa the stools

are generally copious, liquid and sometimes whitish in colour.

In most of the weak and very emaciated cases, the minimum temperature during the day used to be 97°F, sometimes even 96°F, and unless there was some other complication the maximum temperature used to be varying between 98° and 99°F. In some cases the maximum used to rise up to 102°F and in a few cases even up to 103° or 104°F. In almost every case there were variations between the morning and evening temperature of about a couple of degrees.

In most cases the patients complained of perspiration during sleep—the so-called 'Night Sweats'.

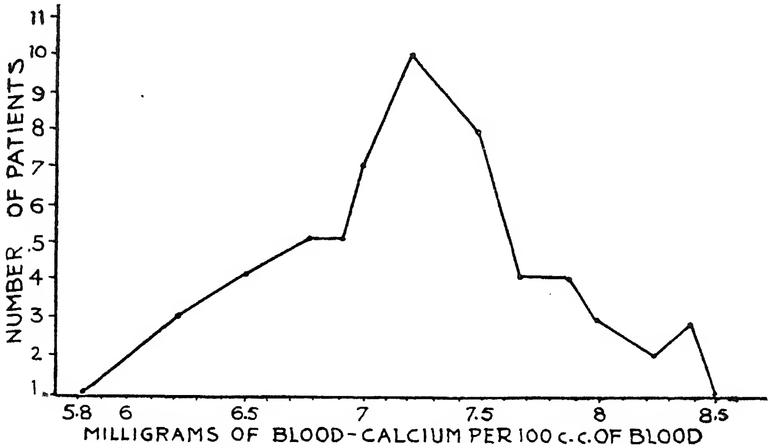


Graph 6.—Graph showing the number of patients and the amounts of blood-calcium among 72 cases in which Tubercle bacilli were found in sputum only. There were 5 more similar cases but their blood-calcium could not be estimated.

There often used to be mild tachycardia the pulse rate in most cases being at least 10 to 15 beats per minute faster than the pulse rate proportionate to the temperature. In very few cases, the pulse rate was normal and within physiological limits. Even if the patient slept well, he always complained of a tired feeling and lassitude on getting up in the morning.

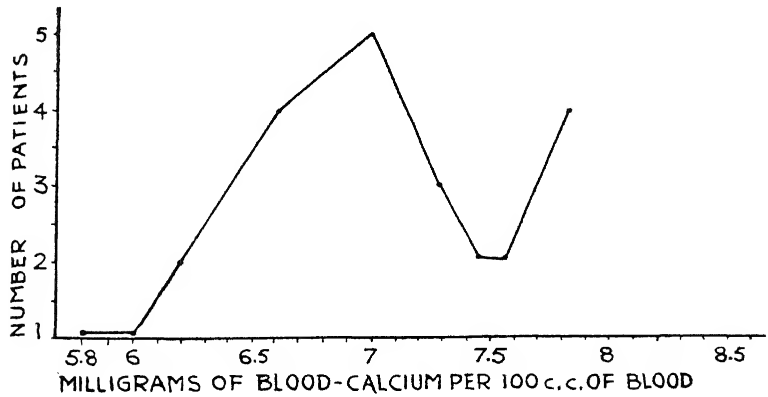
It was possible to estimate the Calcium Content of the Blood in 292 out of the 356 cases investigated. In all these 292 cases, the calcium content was invariably low the minimum being 5·8 mgm. per 100 cc., and the maximum being 8·6 mgm. The largest percentage of cases showed the calcium content of the blood to be 7·4 mgm.

per 100 cc. (Graph 4). Out of these 292 cases, in 124 no Tubercle Bacilli were found either in sputum or fæces (Graph 5); in 77 cases Tubercle Bacilli were found in sputum only (Graph 6); in 64 cases



Graph 7.—Graph showing the number of patients and the amount of blood-calcium among 60 cases in which Tubercle bacilli were found in fæces only. There were 4 more similar cases but their blood-calcium could not be estimated.

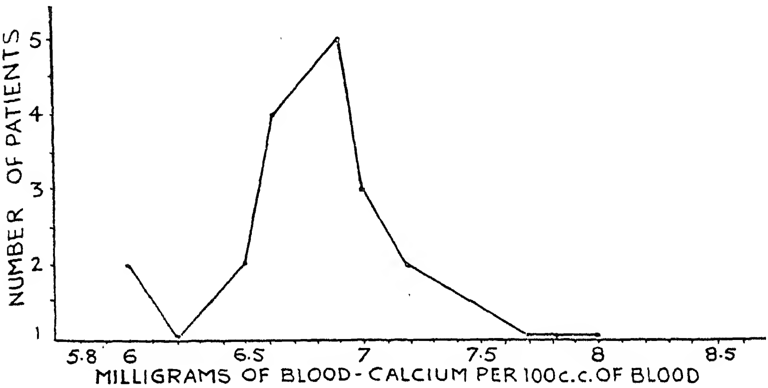
Tubercle Bacilli were found in fæces only (Graph 7) and in 27 cases Tubercle Bacilli were found both in sputum and fæces (Graph 8). Graph 9 shows the calcium content of the blood in cases in which



Graph 8.—Graph showing the number of patients and the amount of blood-calcium among 24 cases in which Tubercle bacilli were found both in sputum and fæces. There were 3 more similar cases of which the blood-calcium could not be estimated.

autopsies were available. The calcium content was diminished in all cases, the average range being 7 to 7·3 mgm. per 100 cc. in the majority of the cases investigated.

The stools were examined in all these 356 cases but Tubercle Bacilli were found in 96 cases only. Out of the 96 cases Tubercle Bacilli were found in the sputum also among 35 cases. In most cases in which the Tubercle Bacilli were found in fæces, the patients had diarrhœa. The reaction used to vary, sometimes being acid, sometimes alkaline. Fresh blood was rarely present. Undigested starch and other food particles were often seen and sometimes large number of fat globules was also seen. In some cases secondary infection was also present, cysts of Entamœba hystolytica and ova of intestinal parasites being found.



Graph 9.—Graph showing the number of cases and the amount of blood-calcium estimated ante-mortem among cases in which autopsies were subsequently available. It was possible to get autopsies in only 22 cases from among the 292 cases in which blood-calcium was estimated. Among the other autopsies studied, blood-calcium estimations were not done (ante-mortem).

Blood examination showed a picture of secondary anæmia. The W. B. C. count varied between 5 and 10 thousand per c. mm. in most cases. The differential count often showed some increase of Lymphocytes while it was sometimes accompanied by a slight increase of Hyalines and Eosinophiles, probably due to old Malaria and helminthic infection.

On examination of the gastric contents after a test meal, it was found that these patients generally had a diminished secretion of free HCl (Hypochlorhydria). Combined acidity was also diminished. In most of the cases investigated, organic acid or blood was not detected. (Refer to table 1.).

Table 2 gives details of the cases in which laparotomies were performed and the diagnosis confirmed. In these cases, the signs and symptoms suggested the diagnosis of Tuberculosis, but there was not a single clinical or laboratory finding sufficient to clinch the diagnosis. In all these cases there was absolutely no evidence of the

Tuberculosis of the lungs, otherwise the Surgeons probably would not have touched them. This table 2 is a sample of findings of all the cases investigated, though it was neither possible nor permissible to perform laparotomies in other cases.

The post-mortem evidence also confirms the same findings, though naturally such cases are advanced and complicated ones.

CONCLUSIONS

Abdominal Tuberculosis, particularly of the intestines and mesenteric glands, is a far more common condition than is generally thought of or suspected.

Contrary to common belief and the teaching of some books, even in adults, evidence of pulmonary tuberculosis is not a *sine qua non* for the diagnosis of abdominal tuberculosis. There are cases in which there are no signs or symptoms in lungs suggestive of Tuberculosis throughout the illness.

The earliest and invariable symptoms are those of anorexia, dyspepsia, irregularity of bowels and gradual loss of weight. Often there is some dull-aching pain without any relation to food.

There is often a difference of about 2°F between the morning and evening temperature.

The pulse is always faster than the rate proportionate to the temperature.

Tubercle Bacilli may be found in fæces, particularly if the patient has diarrhœa. In some cases even after repeated examinations, Tubercle Bacilli may not be found. Simply because the enemy is not sighted, action and precaution must not be deferred.

In the cases investigated, blood-calcium was invariably diminished and I would request those who have greater opportunities for observations and research in big public hospitals to find out whether low calcium content precedes or follows Tubercular infection and whether periodical examinations of the blood for calcium content of these patients would be a guide to determine the response and prognosis of these cases.

In the present state of our ignorance, reliance must be placed on symptoms and clinical findings only, for early diagnosis. Laboratory findings are excellent aids but there is not a single laboratory finding that is pathonomonic of the disease except the demonstration of the Tubercle Bacilli. To postpone the diagnosis till that finding, would be like a mariner awaiting the report of that Meteorological depart-

ment which forecasts the weather and gives warning of the storm only when the ship is actually tossing up in the sea in the midst of a cyclone.

I am obliged to Lieut-Colonel S. S. Vazifdar, Superintendent and Senior Physician, Sir J. J. Hospital and to Major S. L. Bhatia, Dean, and Professor of Physiology, Grant Medical College, for giving me during the period 1922-29 all facilities in the wards of the J. J. Hospital and the Physiology Laboratories of the Grant Medical College. I have also to thank Dr. N. W. Kulkarni and Dr. J. D. Dundas for their help.

TABLE 2.

Clinical and Laboratory findings in cases of Abdominal Tuberculosis in which Laparotomies were performed.

Serial No.	Initials.	Blood Calcium. per 100 c.c.	Blood Count.	Examination of: Sputum.	Examination of: Fæces.	Gastric Analysis expressed in terms of N/10 NaOH per 100 c c. after Ewald test meal.: Free HCl.	Acidity. Total.	Acidity. Combined.	Organic Acids.	Pulmonary signs and symptoms.	Abdominal signs and symptoms.	Findings at laparotomies.
1	R.N.P.	7·4, mgrms.	R.B C. 2,528,000, and W.B.C. 5,000, per c.mm. Hæmoglobin 50%. Polymorphs 60%. Hyalines 8%. Lymphos 32%. Eosinos 1%. Marked Anisocytosis and Poikilocytosis present.	No T.B. found	No Ameba or cysts found. Few ova of Trichocephalus disper seen. No T.B.	10 c.c.	18 c.c.	28 c.c.	Absent	No signs, and symptoms, present.	Anorexia for about six months. Chronic constipation present. Dyspepsia of long duration. A small lump felt at the umbilicus.	Mesenteric glands enlarged and matted together. Tubercles seen on the mesentery. Adhesions formed all over.
14	V.N.B,	7·1, mgrms.	R.B.C. 3,604,000, and W.B.C. 6250, per c.mm. Hæmoglobin 70%. P. 62%, L. 27%, H. 9%, E. 2%. Microcytic Anisocystosis and few Poikilocytes present. No M.P.	No T.B. found.	No T. B. found. Ascaris ova seen. No Ameba or cysts found.	8 c.c.	22 c.c.	30 c.c.	Absent	No signs in the lungs, cough due to pharyngitis.	Irregular bowels, dull pain in the abdomen without any relation to food. No lump felt anywhere. Abdomen shows no rigidity or resistance anywhere.	Tubercles on the mesentery seen. Adhesions all over. Caecum bound by adhesions. Excision not possible.
62	L.M.S	7·2, mgrms.	R.B.C. 3,156,000, and W.B.C. 6250, per c.mm. Hæmoglobin 70%. No M.P. P. 59%, L. 31%, H. 8%, E. 2%. Anisocystosis and Poikilocytosis present.	No T.B. found.	No T. B. found. No Ameba, cysts or ova found.	Gastric contents diluted while taking them out. Free HCl present. Organic acids absent.				No signs or symptoms.	Vague dull aching pain in the abdomen for the last few months. Dyspepsia and history of diarrhoea alternating with constipation.	Tuberculosis of the peritoneum with involvement of the mesenteric glands.
64	T.M.	7·0, mgrms.	R.B.C. 3,604,000, and W.B.C. 5000, per c.mm. Hæmoglobin 60%. No M.P. P. 63%, L. 29%, H 7%, E 1%. Slight Anisocytosis and Poikilocytosis present.	No T.B. found.	No T. B. found. No Ameba, cysts or ova found. Mucus seen.	20 c.c.	35 c.c.	55 c.c.	Absent	Harsh breathing at both apices. No foreign sounds heard.	Anorexia and chronic constipation Caecum palpable and tender. Occasional dull pain present.	Tuberculosis of the caecum and mesenteric glands seen. Adhesions all over. Tubercles over the mesentery seen.
111	G.C.P.	7·5, mgrms.	R.B.C. 3,648,000, and W.B.C. 3750, per c.mm. Hæmoglobin 70%. No M.P. P. 63%, L. 27%, H. 9%, L. 1%. Slight Anisocytosis and Poikilocytosis present.	No T.B. found.	No T. B. or Ameba, cyst ova found. Benzidin test positive.	Could	not	be	done.	Rhonchi heard all over. No dullness elicited anywhere.	Pain and swelling of abdomen. Abdomen tense and retracted History of chronic constipation, sometimes vomiting present.	Peritoneum studded with tubercles all over. Intestines bound down by adhesions. Mesenteric glands enlarged.
175	S.G.	6·9, mgrms.	R.B.C. 2,712,000, and W.B.C. 5000, per c.mm. Hæmoglobin 50%. No M.P. P. 62%, L. 28%, H. 8%, E. 2%. Marked Anisocytosis and Poikilocytosis present. Van-den Burgh's test Indirect Positive.	No T.B. found.	No T. B. found. No Ameba, cysts or ova found. Benzidin test positive.	18 c.c.	21 c.c.	39 c.c.	Absent	Few rhonchi all over, no impairment of note. Throat congested.	Anorexia, constipation and pain all over abdomen. Tenderness in the right hipochondriac region. Sometimes nausea but no vomiting. Mesenteric glands palpable and tender.	Ileum studded with miliary tubercles to the extent of three feet. Caecum tuberculous. Appendix healthy and retro-caecal. Tabes Mesenterica present. Tuberculous masses on the mucosa few inches apart showing tuberculous ulceration within.
238	H.N.	6·7, mgrms.	R.B.C. 2,924,000, and W.B.C. 5000, per c.mm. Hæmoglobin 55%. P. 64%, L. 31%, H. 5%, E. nil. Anisocytosis and Poikilocytosis seen.	No T.B. found.	No T. B. found. No Ameba, cysts or ova found. Lamblia Intestinale seen.	19 c.c.	24 c.c.	43 c.c.	Absent	Harsh breathing present V. F. and V. R. normal. Percussion note normal.	Pain in abdomen more marked in the umbilical area. Pain worse after food sometimes relieved by vomiting, McBurney's point tender. Mesenteric glands palpable and tender, bowels constipated, P.R. reveals no tumour and tenderness.	Small yellowish tubercles scattered in groups on the walls of the intestines. Some strictures in the intestines also noticed.
242	K.H.	7·3. mgrms.	R.B.C. 2,268,000, and W.B.C. 3750, per c.mm. Hæmoglobin 40%. P. 63%, L. 29%, H. 8%, E. nil. Microcytic anisocytosis and punctate basophilia present. Few Poikilocytes seen. Benign Tertain Malarial parasites found.	No T.B. found.	No T.B. found. No Ameba, cysts or ova found.	10 c.c.	20 c.c.	30 c.c.	Absent	No signs or symptoms present.	Loss of appetite, dull-aching pain round about umbelicus and epigastrium, without any relation to food. Tendency for looseness of bowels. No lump felt anywhere.	Intestines studded with milliary tubercles. Mesenteric adhesions present. Matting of the mesenteric glands.
300	M.U	7·0, mgrms.	R.B C. 3,284,000, and W.B C. 4250, per c.mm. Hæmoglobin 60%. P. 61%, L. 31%, H. 7%, E. 1%. Few Poikilocytes seen. No Malarial parasites found.	No T.B. found.	No T B found. No Ameba or cysts found. Ascaris ova found. Benzidin test positive.	14 c.c.	22 c c.	36 c.c.	Absent	Dry hacking cough without expectoration. Pharyngitis present. No signs in lungs.	Appetite markedly diminished for the last few months. History of chronic constipation. Abdomen sunken and rigid. No tenderness present.	Peritoneum studded with tubercles all over. Mesenteric glands matted and enlarged.
345	M.P.	6·9, mgrms.	R.B.C. 2,172,000, and W B.C. 3750, per c.mm. Hæmoglobin 40%. P. 62%, L. 32%, H. 5 %, E. 1%. Macrocytic anisocytosis and Poikilocytosis seen. Polychromasia present. Van den Burgh's test—Indirect Positive.	No T.B. found.	No T.B. found. No Cysts, Ameba or any ova found. Mucus present.	24 c.c.	20 c c.	44 c.c.	Absent	No signs or symptoms.	Started with aneroxia, constipation and dull pain in the abdomen, more marked in the Iliac fossa and near umbelicus. No lump felt in the beginning nor any tenderness present. After a year or more, there was pain more marked after food, sometimes relieved by vomiting. Caecum now palpable and slightly tender. Mesenteric glands palpable.	Peritoneum studded with tubercles. Adhesions formed all over. Stricture produced by these bands. Viscera fixed. Caecum tuberculous. Excision not possible. Lateral anstomosis made between loops on either side of the stricture.

TABLE 1.

Gastric Analysis after Test-meal.

Number and initials.	Expressed in terms of N/10 NaOH			Organic acidity.	Blood etc.	Remarks.
	Free HCl	Combined acidity.	Total acidity.			
1 R.N.P.	10 c.c.	18 c.c.	28 c.c.	Absent	Nil.	Most of the cases showed diminished HCl. Occult Blood not detected. Oppler Boas Bacilli or any other Pathogenic organisms not seen.
11 B.R.	12 c.c.	30 c.c.	42 c.c.	Absent	Nil.	
17 B.G.	17 c.c.	32 c.c.	49 c.c.	Absent	Nil.	
57 J.C.	22 c.c.	46 c.c.	68 c.c.	Absent	Nil.	
60 S.S.	17 c.c.	40 c.c.	57 c.c.	Absent	Trace present	
64 T.M.	20 c.c.	35 c.c.	55 c.c.	Absent	Nil.	
93 N.A.	15 c.c.	25 c.c.	30 c.c.	Absent	Nil.	
134 S G.	15 c.c.	25 c.c.	40 c.c.	Present	Nil.	
144 R.B.	17 c.c.	36 c.c.	53 c.c.	Absent	Nil.	
175 S.G.	18 c.c.	21 c.c.	39 c.c.	Absent	Nil.	
196 T.D.	24 c.c.	22 c.c.	46 c.c.	Absent	Nil.	
211 E.P.	20 c.c.	24 c.c.	44 c.c.	Absent	*Streak of bloodseen*	
238 H.N.	19 c.c.	24 c.c.	43 c.c.	Absent	Nil.	
242 K.H.	10 c.c.	20 c.c.	30 c.c.	Present	Nil.	
251 F.M.	15 c.c.	25 c.c.	40 c.c.	Absent	Nil.	
254 N.L.	16 c.c.	30 c.c.	46 c. c.	Absent	Nil.	
282 J.H.	20 c.c.	30 c.c.	50 c.c.	Absent	Nil.	
300 M.U.	14 c.c.	22 c.c.	36 c.c.	Absent	Nil.	
306 K.M.	9 c.c.	14 c.c.	23 c.c.	Absent	Nil.	
310 H.R.	31 c.c.	28 c.c.	59 c.c.	Absent	Present	
325 C.J.	18 c.c.	27 c.c.	45 c.c.	Absent	Nil.	
339 G.B.	12 c.c.	25 c.c.	37 c.c.	Absent	Nil.	
345 M.P.	24 c.c.	20 c.c.	44 c.c.	Absent	Nil.	
356 V.N	16 c.c.	28 c.c.	44 c.c.	Absent	Nil.	

24 cases.

Cases showed Hypochlorhydria.

SOME COMMON HYDROMEDUSÆ OF THE BOMBAY HARBOUR

(*With 3 plates and 1 text-figure.*)

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CONTENTS : Introduction—Steenstrupia bigelowi—Phortis ceylonensis—Phialucium virens—Aglaura hemistoma—Liriope tetraphylla—Solmundella bitentaculata—Concluding Remarks—Acknowledgments—References—Explanation of figures.

INTRODUCTION

The Hydromedusæ described in this paper were picked out of the macroplankton periodically collected by us in the Bombay Harbour from October 1932 to February 1934. During this period the plankton was collected once a week for half an hour at least, by means of a muslin net towed at the surface of the water usually from a sailing boat. As during this preliminary investigation of the local planktonic organisms sufficient time was not available for studying in detail the common forms while alive, these surface tows have been repeated since then and we hope to continue them for studying the common planktonic organisms of different phyla and classes available in Bombay.

After going over the literature connected with the few forms being described here, it was noticed that their detailed descriptions were scattered through various journals and voluminous reports of many scientific exploring expeditions published during a period of over a hundred years, and further that no single description of these completely suited the local forms as those species show a wide range of variation in their morphology and as some of these descriptions are based on scanty and preserved material. We have therefore described the local specimens of these species and included in this paper illustrations of their living and anæsthetized local specimens, kindly drawn for us by Mr. D. C. Joglekar, artist in the Department of Zoology of the Royal Institute of Science, Bombay.

STEENSTRUPIA BIGELOWI (MAAS)

Plate I, fig. 3.

Euphysora bigelowi, Maas, 1905, Craspedoten Medusen der Siboga Expedition, Monog. 10, p. 7, taf. 1, figs. 1-3.

External Features :—It is a small colourless medusa with its radially symmetrical pyriform bell being about 3-5 mm. high and 2 mm. wide. Its brownish or yellowish manubrium is clearly seen through the thin transparent wall of the bell and it often extends from the top to the base of the bell-cavity, although its length and shape are highly variable. The bell is produced at the top into a short conical glassy process without any structures inside. Arranged regularly round the margin of the bell there arise 4 tentacles, three of which are short, thick and rudimentary and the forth long, slender and highly contractile. The short and tapering tentacles are nearly as long as the bell is high, and have smooth colourless surface except for a line of reddish granules along their axes, situated in their core. The fourth tentacle is thread-like and bears rounded bodies or batteries of nematocysts at intervals. The number of these nematocyst-warts may vary from 7 to 35 in animals of nearly equal size. The velum is narrow and muscular.

Internal Organs : The mouth situated at the end of the manubrium is bounded by a narrow annular lip and is highly distensible. It leads into a spacious stomach in the manubrium which is sometimes found filled with oil-globules. At the junction of the manubrium with the bell the stomach is continued into four linear canals which radiate towards the periphery to join the circular canal lying along the margin of the bell. Both the circular and radial canals are colourless and indistinct in living specimens but become well defined in preserved ones. Under the microscope a few red granules are seen scattered in the lining of the radial canals. The tentacles start from the junctions of the radial canals with the circular canal and are hollow. Their axially placed streak of red is due to pigment granules in their endoderm.

The sexes are separate and the gonad developing round the manubrium in its wall surrounds it in the middle and gradually narrowing does not reach its base or mouth. An examination of the sections of a medusa showed that the four free perradial longitudinal lines, mentioned by Maas, were not present. Thus its gonad could not be divided into four interradial zones or gonads.

Occurrence : One or two specimens of this tiny medusa were sometimes found in our tow-nettings from January to April and during March and April they showed well developed gonads. Thus about

fifty specimens were collected and most of them agreed in being of about the same size as that of the medusa drawn and described above.

GENERAL REMARKS. The medusæ described in this paper are provided with a muscular velum partially closing the mouth of the bell and are known as Hydromedusæ. This hydromedusa is further known as Anthomedusa and differs from the rest in having the gonads round the manubrium and in not having any sensory vesicles. The Anthomedusæ are all marine and have been found along coasts and especially in harbours. It is likely therefore to come across some more of them in the vicinity of Bombay.

This medusa was first recorded in 1905 by Maas from the Malay Archipelago as occurring quite commonly and reaching a size three times as large as the Bombay specimens. Further the majority of his specimens had a short blind axial canal extending into the conical process at the top of the bell, while only one of our specimens had a similar axial canal. The axial canal and the larger size of the Malay specimens may be taken as due to growth and specimens of intermediate sizes may be searched for. In this connection it is interesting to find that this medusa has not been observed in Madras Waters during a recent prolonged study of the Hydromedusæ of that locality (Menon). Besides another medusa agreeing with Bombay specimens on all points except the arrangement of the nematocyst-warts on the tentacle has been described by Bigelow as Euphysa tetrabranchia from the Maldive Islands (Bigelow). So far as Bombay and Malay specimens are concerned they form one species, but whether it requires to be divided into two or three races so as to include also the Maldive specimens, only future observations can tell.

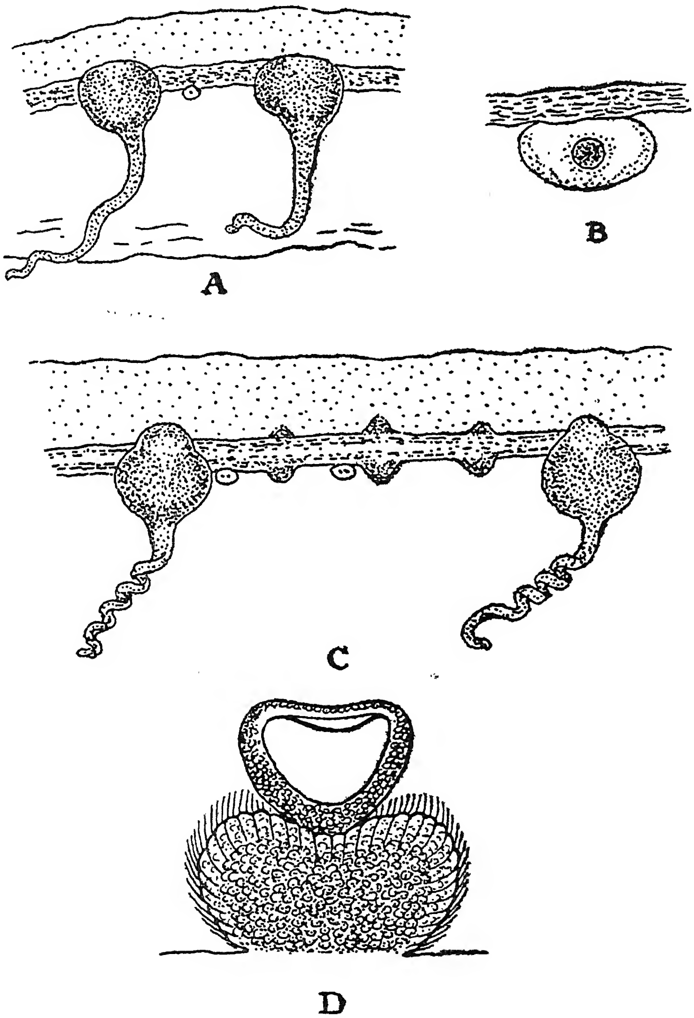
PHORTIS CEYLONENSIS (BROWNE)

Plate I, fig. 2.

Irene ceylonensis, Browne, 1905, Report, Peart Oyster Fisheries, Gulf of Manaar, Suppl. Report No. 27, Roy. Soc. London, p. 140, plate 3, figs. 9-11.

EXTERNAL FEATURES.—This is a thin flat umbrella-like colourless medusa with numerous short marginal tentacles and a central handle-like transparent peduncle ending in a short and distinct manubrium. The bell is really shallow-watch-glass-shaped, being many times wider than high and attaining a diameter of 18 mm. The faintly yellowish manubrium is usually flask-shaped with its wall being produced round the mouth into four folded lips with their edges put into minute folds. The cylindrical peduncle is nearly as long as the radius of the bell and scarcely shows the four radial canals passing along its surface. The number of the tentacles varies with the size of the medusa, the

4 mm. wide medusa having about 28 tentacles and the 16 mm. wide medusa having about 72. These short, slender and tapering tentacles (Text-fig. 1, A) are swollen at their origin from the margin of the bell and these basal bulbs are faintly greenish yellow. Alternating with the tentacles along the margin of the bell are found its sensory organs or the lithocysts (Text-fig. 1, B.). The lithocyst is a thin-



Text-figure 1. Tentacles and Sensory Organs of Hydromedusae. A. Portion of the bell-margin of Phortis ceylonesis with two tentacles and a lithocyst between them ; B. Lithocyst of the same further magnified showing its lithite ; C. Portion of the bell-margin of Phialucium virens showing its tentacles, rudimentary tentacular bulbs, the conical processes of the former two and lithocysts with two lithites ; D. Sensory Club of S. bitentaculata.

walled sac containing usually a small calcareous particle attached to its side. These vesicles are situated midway between the tentacles and are in contact with the circular canal. The velum is very narrow.

INTERNAL ORGANS : The small stomach in the basal part of the manubrium leads into four linear radial canals extending along the length of the peduncle and then radiating along the subumbrellar surface of the bell to the circular canal. Both the circular and radial canals are slender and inconspicuous, but the gonads developing in connection with them are faintly yellowish and extend from the base of the peduncle to the margin of the bell. They appear as the thickings of the lateral walls of the radial canals protruding on the subumbrellar surface.

OCCURRENCE : This scantily pigmented medusa was present in the Bombay Harbour practically throughout the year and was represented by 2 or 3 specimens in each two-netting except in the months of July, August and September, when it was very rare. Larger specimens were found during March and April and they had well developed gonads. About this time of the year some specimens were found with gonads and tentacles partly lost, probably suggesting that those medusæ had shed their reproductive products and were disintegrating.

GENERAL REMARKS : This medusa was first described in 1905 by Browne from a few preserved specimens from the West Coast of Ceylon and was found by Annandale later on in large numbers in a brakish pool at Port Canning in Lower Bengal, where he found its hydroid also. The figure accompanying Annadale's paper makes the bell-cavity much deeper than what has been observed in Bombay specimens either living or preserved.

As this and the next medusa possess gonads on the radial canals and also lithocysts they belong to a large order of Hydromedusæ viz. Leptomedusæ which differ among themselves mainly in having either lithocysts or marginal sensory clubs and in having different numbers of radial canals. This order is represented by 18 species on the Madras Coast (Menon) and we have evidence to the effect that some more Leptomedusæ occasionally visit the Bombay Harbour from the outside.

PHIALUCIUM VIRENS (BIGELOW)

Plate I, fig. 1.

Oceania virens, Bigelow, 1904, Bull. Mus. Comp. Zool. at Harvard College, Vol. 39, p. 252, plate I, figs. 3, 4.

EXTERNAL FEATURES :—This is a colourless watchglass-shaped medusa with many marginal tentacles and a short wide manubrium arising from the middle of the ventral surface of the bell. The dia-

meter of the bell varies from 3 mm. to 16 mm. and its height from 1 mm. to 5 mm. The wall of the bell is firm and thick in the middle making the upper surface of the bell more arched than in the previous medusa. As there is no peduncle the manubrium appears to be a loose portion of the skin surrounding the mouth at the centre of the subumbrellar surface of the bell. The mouth is wide and squarish with its margin produced into four deeply folded lips. The number of tentacles in large specimens comes to between 20 and 25 but at the same time their arrangement on the margin of the bell suggests that there may have been some more in the wide gaps left in between them. The portions of the margin between adjacent tentacles are unequal and contain 2 to 5 rudimentary tentacular bulbs. The tapering slender tentacles can be as long as half the radius of the bell and have large hollow basal bulbs with conical processes extending on the inner side of the circular canal into the gelatinous substance of the bell. These bulbs are coloured bright red inside. The rudimentary tentacular bulbs are of different sizes, are about thrice the number of the normal tentacles and have similar projections on the other side of the circular canal. The number of the lithocysts is also approximately the same as that of the tentacular bulbs but they are irregularly distributed in between them and contain one or two lithites in each.

INTERNAL ORGANS : From the four corners of the squarish stomach start four straight radial canals which meet the circular canal along the margin of the bell. The gonads cover the distal three-fourths of the radial canals and are thicker than those of the former medusa. They hang down vertically from the radial canals as incipient partitions dividing the bell-cavity into four quadrants. They have three to five bright red pigment spots along their length and also the lips of its mouth have radiating dashes of yellowish green.

OCCURRENCE : Although less common than the previous medusa, it is present throughout the year in the Bombay Harbour. Its gonads are seen well developed particularly in the months of March and April.

GENERAL REMARKS : This medusa appears to have a wide range in the tropical parts of the Indian and Pacific Oceans although it inhabits sheltered places along coasts.

AGLAURA HEMISTOMA PÉRON et LESUEUR

Plate I, fig. 4.

Aglaura hemistoma, Péron et Lesueur, 1809, Annals, Mus. Hist. Nat. Paris, tome 14, p. 351 :——Medusæ of the World by Mayer, 1910, Vol. 11, p. 398, plate 49, figs. 4 to 7.

EXTERNAL FEATURES :—It is a tiny colourless cup-like medusa

with its gonads and manubrium hanging down inside from the top and with its marginal, very short, close-set tentacles being hardly visible. The bell is from 1·5 mm. to 4 mm. high and from 1 mm. to 3 mm. wide. Its shape is much variable and in preserved specimens its top may appear either quite flat or hemispherical. Its wall is very thin but firm and muscular, and after preservation appears under the microscope to be provided with numerous ribs. Its subumbrellar surface is produced into a short conical or cylindrical peduncle which is one-fourth the height of the bell and supports the gonads and the manubrium at the end. The manubrium is usually funnel-shaped with the margin of the mouth being produced into 4 pointed lips. The tentacles are about 45, and are very short, solid and tapering. These apparently complete tentacles may be the broken bases of longer ones as considerably longer tentacles have been observed in specimens of this cosmopolitan species from different parts of the world. Its sensory organs or sensory clubs are 8 solid, and minute pimples regularly arranged along the margin of the bell. Each of them is a conical cellular growth containing a calcareous particle inside and covered with some sensory hairs. The velum is relatively broad and muscular and even in preserved and contracted specimens its inner margin extends halfway to the centre and considerably closes the mouth of the bell.

INTERNAL ORGANS : The stomach leads into 8 linear canals which reaching the base of the peduncle bend outwards and go straight along the wall of the bell to the circular canal. The already noticed sensory clubs are situated midway between adjacent radial canals and are adradial in position. Four of the radial canals are along the four principal radii of the bell and the remaining four alternating with them are interradial in position. The eight sausage-shaped gonads are developed in connection with the radial canals at their junction with the manubrium. When fully developed they are quite thick and become as long as the peduncle or the manubrium. The only parts of the medusa which contain any pigment are the gonads and some elongated patches on the manubrium and they are pale yellow.

OCCURRENCE : This medusa suddenly appeared in the Bombay Harbour about the middle of December and similarly disappeared in February. Quite a number of them could be collected in a surface tow during January. A few specimens were collected as late as June suggesting that some of them were lagging behind or had survived their wholesale destruction in the meanwhile.

GENERAL REMARKS : This is a cosmopolitan species found at the surface in warm and tropical seas. It is variable to some extent in size and shape, in the relative length of the peduncle and in the

shape of the gonads. Accordingly as many as eight species of this genus have been described from different parts of the world but in the opinion of Mayer all of them constitute a single species of which they may be looked upon as local races or at the most varieties.

An interesting point about this medusa is that one of its varieties—Aglausa octagona, probably another species,—is described and was found by Bigelow from a depth of 100 fathoms in the Maldive Islands.

LIRIOPE TETRAPHYLLA (CHAMISSO et EYSENHARDT)

Plate II, fig. 6 ; plate III, fig. 7.

Geryonia tetraphylla Chamisso et Eysenhardt, 1821, Nova Acta Phys. Med. Acad. Leop. Carol., tome 10, plate 27, fig. 2 ; Liriope tetraphylla, Gegerbeur, Medusæ of the world by Mayer, 1910, Vol. 11, p. 418.

EXTERNAL FEATURES:—This large, active and solidly-built colourless medusa has a long conical peduncle and still longer four tentacles. Its bell varied from 6 mm, to 19 mm. in diameter and from 3 mm. to 11 mm. in height. It is nearly hemispherical, although very variable in outline. Its firm gelatinous substance is very thick in the middle of its aboral surface and thins out gradually to the margin of the bell. It also provides an elongated and conical core to its peduncle. The peduncle has a broad base half as wide as the bell at that level and its length is twice the height of the bell. Its manubrium situated at the apex of the peduncle is highly variable in its outline. It has a four-sided mouth with nodules of nematocysts along its margin. According to the state of contraction its wall may be rolled back or folded and produced into four pointed lips. Occasionally in a very few preserved specimens the tip of the relatively firmer and less contractile gelatinous core of the peduncle may project out of the contracted and rolled back manubrium and appear as the tongue of this animal. There are four slender, hollow tentacles arranged regularly along the margin of the bell and they are twice or thrice as long as the bell-diameter. They are provided with close-set rings of nematocysts and after preservation they appear rough and short with blunt ends and unequal lengths. These active and easily noticed tentacles are really secondary and are developed subsequently to eight very short and slender primary ones which are usually lost. Four of them are perradial and starting at the base of the long tentacles bend aboralwards along the exumbrellar surface of the bell. The other four are similarly directed and are interradial in position. The eight sensory lithocysts are embedded in the wall of the bell at the bases of these 8 short tentacles. Each of them (Text-fig. 1, D) is a rounded cellular

mass containing a single concretion. The velum is broad and muscular.

INTERNAL ORGANS : The stomach is long and sac-like. The four radial canals are fairly broad and alternate along the periphery of the peduncle with four interradial, longitudinal muscle bands, which bifurcate at the base of the peduncle and its two ends curve outwards. The radial canals similarly bending outwards go straight to the circular canal, which is also equally spacious, if not more, and has up to seven, centripetal, broad, blindly ending diverticula in each interradial quadrant. The number of these finger-like blind canals usually begins with three in very small specimens and increases with the age and size of the animal. The longest and oldest of those is interradial in position and the remaining six, though of unequal lengths are symmetrically arranged on its sides. The leaf-like gonads develop symmetrically on both the sides of the radial canals in their subumbrellar parts and are triangular with their apices pointing towards the margin of the bell. As they increase in expanse their angles become rounded and the sides concave. In well developed gonads their blunt and rounded apices appear to rest on broadened perradial diverticula of the circular canal. Even in our largest specimen the angles at the base of the inverted triangular gonads did not meet the similar angles of the adjacent gonads at the level of the top of the bell-cavity. The ectoderm along the margin of the bell is thickened to form an annular ledge and contains numerous nematocysts. It sends upwards along the exumbrellar surface similar, short and slender radial and interradial processes called peronia. This medusa is very scantily coloured and a rosy tinge is found on its tentacles, gonads and the nematocyst warts round the mouth.

OCCURRENCE : This medusa is commonly found from January to May in the Bombay Harbour. Once in April in one surface tow as many as 75 specimens were found.

GENERAL REMARKS : It is one of the very widely distributed oceanic medusæ found in all tropical oceans—Indian, Atlantic and Pacific. According to Mayer as many as eleven distinct species of this genus described from different localities should be combined into a single species viz. Liriope tetraphylla. In other words this species is capable of so many variations depending on the differences in its colour, the size and shape of the bell and of the gonads.

This and the last Hydromedusa are known as Trachymedusæ and differ from the Leptomedusæ in the appearance and development of their sensory organs—lithocysts or sensory clubs.

SOLMUNDELLA BITENTACULATA (QUOY et GAIMARD).

Plate II, fig. 5 ; plate III, fig. 8.

Charybdea bitentaculata, Quoy et Gaimard 1833, Voyage de l'Astrolabe, tome, 4 p. 295, planche 25, figs. 4 and 5 ; Solmundella bitentaculata Browne, Medusæ of the World by Mayer, Vol. 2, p. 455, plate 54 figs. 1-3.

EXTERNAL FEATURES :—It is an active colourless conical medusa provided with two tentacles and with neither peduncle nor manubrium. This easily recognisable medusa may be 12 mm. in height and 8 or 9 mm. in bell diameter at its oral end. Its inverted bowl-shaped bell has a rounded top and a very shallow bell-cavity with a very thick aboral wall between. Its apex is neither sharp-edged nor keel-shaped as observed by some naturalists. The dome of the bell is hardly elongated in the plane of its tentacles. Its oral outline, although notched in the tentacular axis is quite circular and not elongated. The mouth of this medusa is a circular opening situated in the centre of the flat top of its bell-cavity and opening into its wide and flat stomach. It is surrounded by an annular lip capable of being everted and projecting as a short tube or of closing the oral aperture to a slit. Sometimes in preserved specimens the lip is seen as a narrow rim round its wide circular mouth. Its two whip-like tapering tentacles are about three-times the bell-diameter in length and they emerge out of the bell at a level dividing its aboral thickness into upper and lower halves. Under the microscope their enlarged and vacuolated axial cells give them an appearance of being closely segmented. This thickened axis penetrating obliquely downwards and inwards the gelatinous substance of the bell and reaching the aboral wall of the stomach ends in a horizontal conical root. From the notch at the either side of the oral rim of the bell ascends a shallow groove which terminates above the tentacle. Along the base of this furrow a peronium is situated which starts from the ectodermal annular thickening round the velar margin of the bell. There are also two more short peronial stands starting midway between them from the margin of the bell. But these two are inside the gelatinous layer of the bell-wall and in connection with these no grooves are noticed. The tentacle at its base is supported by inner and outer or axial and abaxial lamellar muscular strands helping its powerful oar-like movements. In some specimens the axial muscular lamellæ are joined by a fibre-like strand across the gelatinous thickness of the bell. There are 16 to 32 free sensory clubs along the ectodermal annular thickening round the margin of the bell. Each of them is a short cellular column containing a single terminal concretion and mounted on a rounded cellular base

(Text-fig. 1, D.) The velum is quite broad and powerful with its circular muscles.

INTERNAL ORGANS : The mouth leads into its wide and flattened stomach which is produced into 8 gastric pouches or outpockets. They are symmetrically arranged on either side of the tentacular grooves and the four of each side are further divided into two pairs by the short peronial strand penetrating their middle partition. They are almost rectangular and extend close to the margin of the bell. The gonad starts to develop in the subumbrellar walls of these pouches and extending centripetally forms a wide ring round the mouth. The bell is quite colourless and only a broad distal part of the tentacles appears bright yellow under the microscope.

OCCURRENCE : This medusa is quite commonly found from November to May. In March and April they are numerous and of all sizes. About this time the gonad is well developed and its microscopic young ones may be found inside the bell.

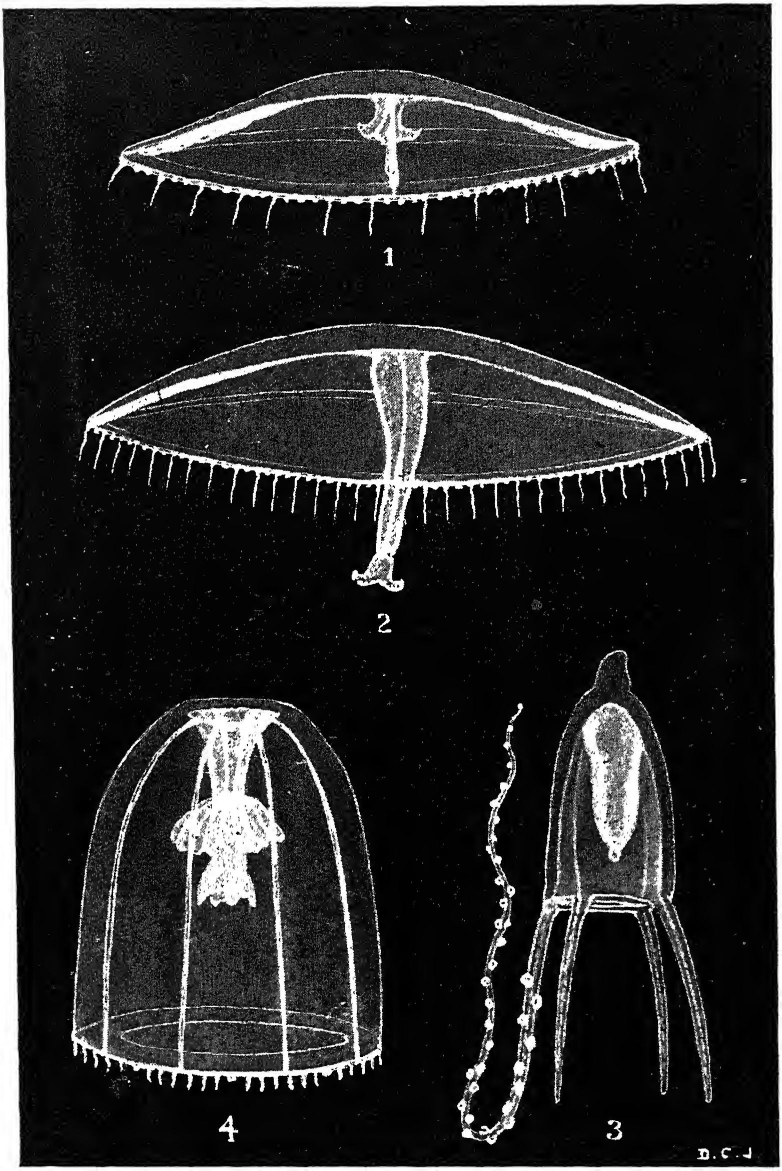
GENERAL REMARKS : This is one of the most widely distributed medusæ ranging from the North Atlantic to the Antarctic through the tropical Indian and Pacific Oceans, living at a temperature varying from 27° C to — 1° C and in depths ranging from 1500 fathoms to the surface. This hydromedusa belongs to the order of Narcomedusæ as the margin of its bell is cleft by the two shallow tentacular grooves. These gaps are bridged over by the extensions of the velum which is undivided.

CONCLUDING REMARKS

The Bombay Harbour is formed by the confluence of three long creeks at their opening into the Arabian Sea. These creeks have many lateral bays and feeder creeks thus considerably increasing the inland protected area of salt and brakish water where hydroids and other fixed colonial organisms could thrive undisturbed. Thus the Bombay Harbour provides a meeting ground for numerous inshore and offshore marine organisms carried about by tides and currents.

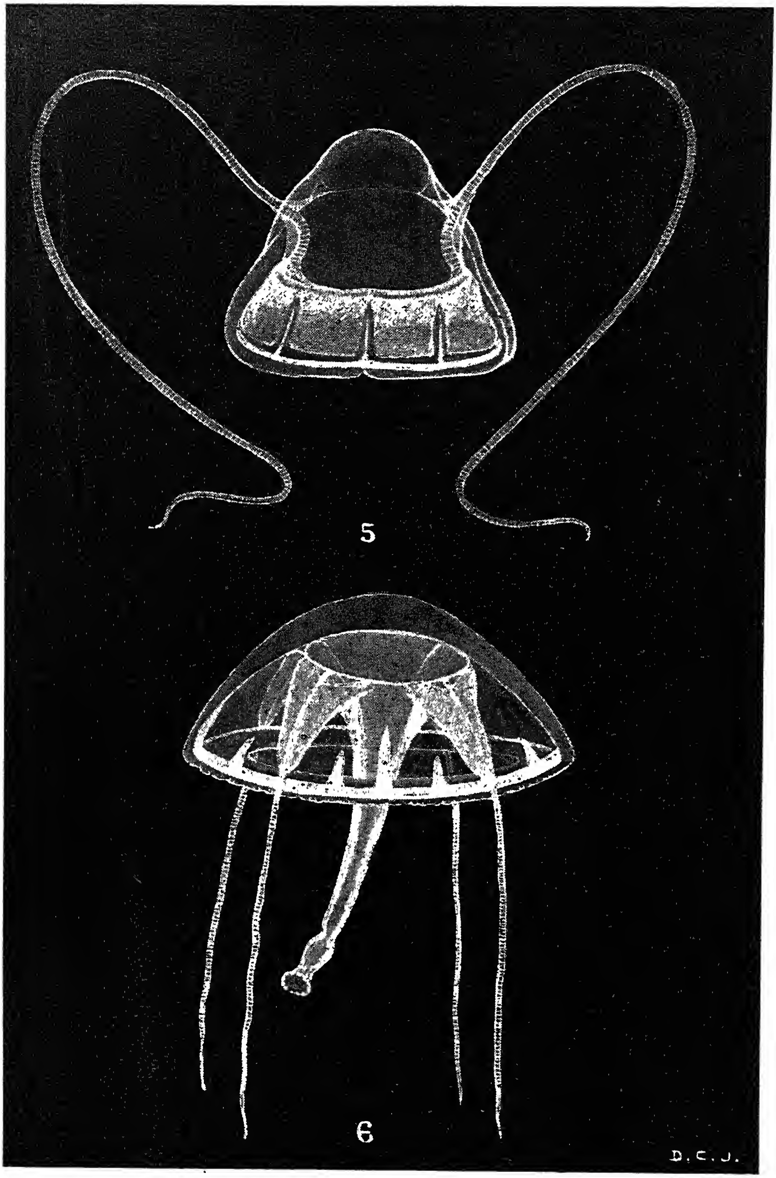
The present account of the Hydromedusæ of the Bombay Harbour is obviously incomplete as a few more equally or less common forms are likely to be discovered in this area. Our collections have shown that at least Aequorea parva of Browne requires to be included here as it was found during September and October. But it could not be described here as no living specimen of this species was found during the preparation of this paper.

Of the six medusæ described in this paper the first four are inshore or coastal forms living either in harbours, creeks or in the sea not far from the coast. These are usually developed on, and freed



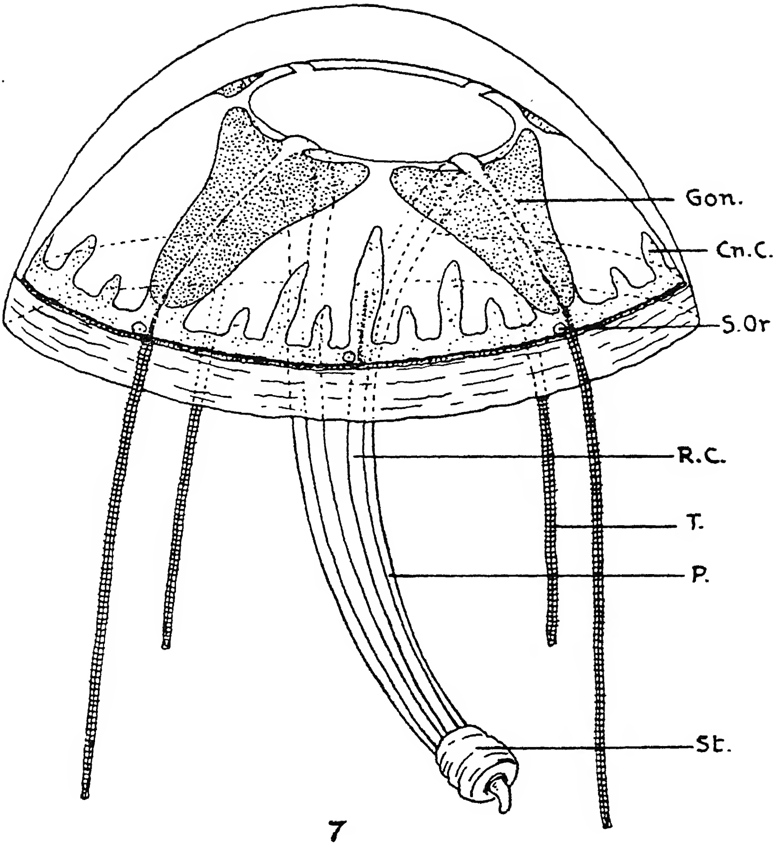
BOMBAY MEDUSAE DRAWN FROM LIFE

Fig. 1. Phialucium virens X 6
Fig. 2. Phortis ceylonensis X 5.
Fig. 3. Steenstrupia bigelowi X 10.
Fig. 4. Aglaura hemistoma X 12.



BOMBAY MEDUSAE DRAWN FROM LIFE

Fig. 5. Liriope tetraphylla X 7.
Fig. 6. Solmundella bitentaculata X 3.



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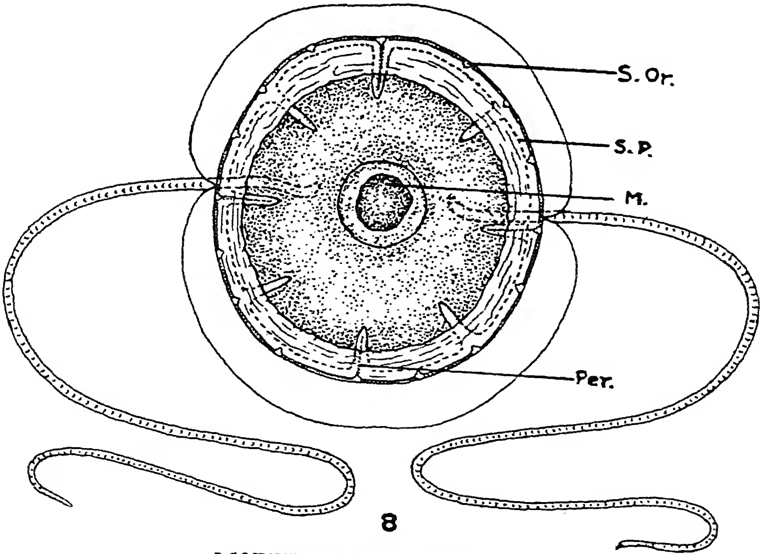

8

MORPHOLOGY OF MEDUSAE

Fig. 7. Diagrammatic side view of L tetraphylla. Cn. C. centripetal canal ; Gon. gonad ; P. peduncle ; R. C. radial canal ; S. Or. sensory organ ; St. stomach. T. tentacle.

Fig. 8. Diagrammatic oral view of S. bitentaculata. M. mouth ; Per. peronium ; S. O sensory club ; S. P. outpocket of the stomach.

from fixed colonial hydroids living in such places. Including both common and rare forms of this kind thirty species have been described from Madras (Menon), thirteen from the West Coast of Ceylon (Browne) and six from the Maldive and Laccadive Archipelagoes (Browne). It is quite likely therefore that some more Antho-and Lepto-medusæ will be discovered in this area by further investigation. The last two forms, on the contrary, are not only offshore but oceanic medusæ being widely distributed over the open oceans. Of this category only one or two may be met with in the Bombay Harbour as only two or three more forms have been described from the areas mentioned above.

ACKNOWLEDGMENTS

We take this opportunity to express our thanks to Dr. T. S. Wheeler, Principal and Prof. P. R. Awati, Professor of Zoology, Royal Institute of Science, Bombay, for providing us with funds for collecting plankton and giving facilities for work. We must also thank Dr. Baini Prasad for lending us books from the library of the Zoological Survey of India at Calcutta and Lt. C. H. Clark R. N. R. for giving us all necessary help when during the rainy season we used our tow-nets from the Indian Mercantile Marine Training Ship "Dufferein".

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THE ANATOMY OF DENDROSTOMA SIGNIFER SELENKA ET DE MAN 1883

(IN TWO PARTS)

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Part I (with 2 plates and 8 text-figures).

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CONTENTS—1. Introduction; 2. External Characters; 3. Habits; 4. General Anatomy; 5. Body-wall; 6. Coelomic Fluid; 7. Digestive System.

INTRODUCTION.

On finding that specimens of Dendrostoma signifer are not rare on the coast of the Bombay Island and that this species alone represents in Bombay the interesting Sipunculoid worms we thought it advisable to work out its anatomy in detail. After going through the literature it became evident that the anatomy of this worm showed some important deviations from that of other Sipunculoids already described by other workers. It is therefore attempted in this paper to describe in detail the anatomy of this species and to record our observations on its habits etc.

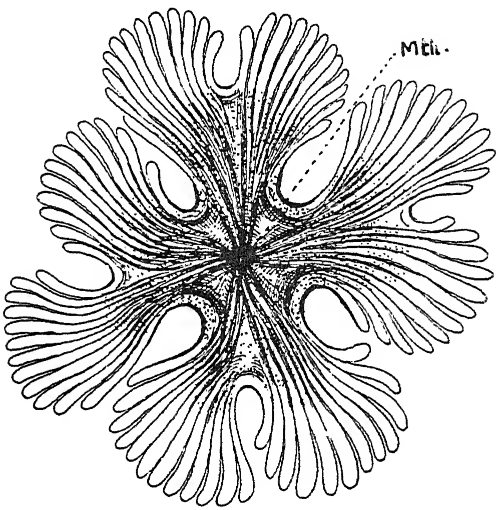
EXTERNAL CHARACTERS.

Dendrostoma signifer is an elongated or bottle shaped worm (Plate I, Fig. 1), being narrow at the anterior and swollen at the posterior end. Its posterior extremity tapers to a point. There is no trace of division of the body into segments. The outline of the body is more or less uniform but it is subject to considerable changes, depending on the state of contraction of the muscles of the body-wall. When fully extended, the animals usually measure from 20 to 25 mms. in length. The diameter of the trunk varies from 6 to 9 mms. The smallest specimen found was about 8 mms. long and 1·5 mms. across its posterior end. Occasionally, specimens of 40 mms. in length are also found.

In order to study the structure of this extremely contractile animal the use of some anæsthetic is necessary and after trying several narcotizing agents Dakin's seawater-glycerine-alcohol (70%) mixture was found to be quite successful. This contains these three in the pro-

portion of 2 : 1 : 1, and requires to be slowly added to the seawater containing the living Dendrostoma. Usually in about 6 hours the animal gets fully extended and becomes quite insensible, whereon it could be injected with and transferred to different fixing fluids according to requirements.

Since the anterior one-fourth of the body is invaginable into its posterior part, the body can be divided into two regions, *viz.*, the introvert and the trunk. The anterior end of the introvert provided with the tentacles and containing the brain is termed the head. When the introvert is extended the tentacles form a bunch of short processes



Text Fig. 1. A diagrammatic view of the expanded tentacles at the oral end. X 24.

surrounding the mouth and projecting forward and outwards in their expanded condition. There are ninety-six short and simple tentacles arranged in four groups at the periphery of a fleshy evaginated membrane—the circumoral membrane. At its centre the narrow oval mouth (Fig. 1 mth) of this animal is situated and from its edge there radiate numerous ridges and grooves towards the bases of the tentacles. The mouth is not usually visible, being contracted and hidden inside the close-set tentacles. Each tentacular filament is a blunt digitate process somewhat flattened dorsoventrally and provided with a convex aboral and a concave oral surface. The oral surface has a longitudinal ciliated groove.

On the introvert are to be found in younger stages feebly developed hooks but they fall off in adults. Hence there are no hooks in contrast to what has been observed in other Sipunculoids.

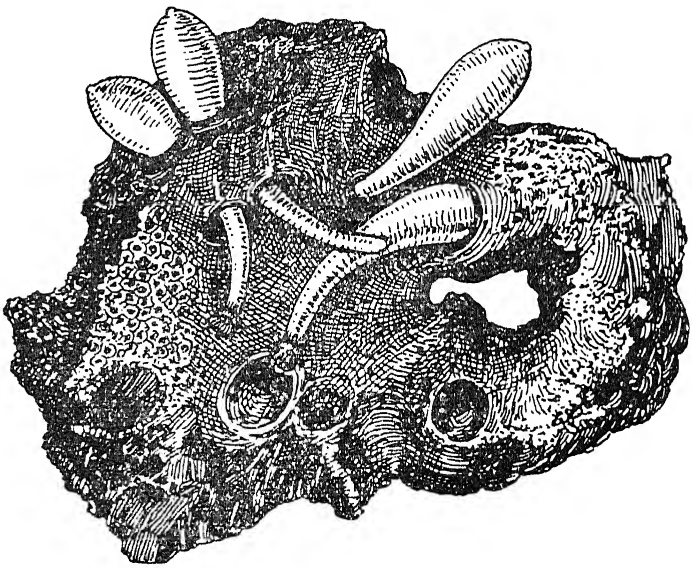
The trunk appears to have a smooth surface but when magnified about ten times it appears to be broken into quadrate areas by shallow longitudinal and transverse grooves. At the centre of each area is found a conical projection with an opening at its apex. These projections are the epidermal organs of the Sipunculoids. The animal has a brownish or greyish colour. At the anterior end of the introvert a deep blud ring or collar can be distinguished. The portion between the collar and the base of the tentacles appears to be greyish-blue while the tentacles are pinkish (Plate 1).

The anus is a median opening on the dorsal surface at about one-fifth the length of the body from the anterior end. The openings of the brown tubes are paired and laterally situated on the ventral surface a little behind the level of the anus.

The sexes are separate, but they cannot be distinguished by any external characters. The colour, size and shape are exactly similar in both the sexes.

HABITS.

Species of Dendrostoma are usually found along the rocky shores of the tropical seas. They inhabit either natural rock fissures or tunnels in the coral rocks (Fig. 2.), situated between the tide-marks.



Text Fig. 2. The animals as seen in their natural position in the coral Rocks.

They do not appear to be gregarious in their habits although a few of these are occasionally found living together.

Dendrostoma signifer is a very sluggish animal in its movements. It can very slowly crawl about by thrusting forward the introvert and after fixing it dragging the body from behind. The only visible movements which are exhibited by the animal are confined to its tentacles and the introvert. The tentacles are often spread out widely exploring the surface in all directions. They are also used in removing the particles of sand in their neighbourhood. At intervals the introvert is taken out fully or withdrawn inside. Accompanying the elongation and shortening of the introvert the rest of the body shows alternate contraction and expansion due to the action of the longitudinal and circular muscles of the body-wall.

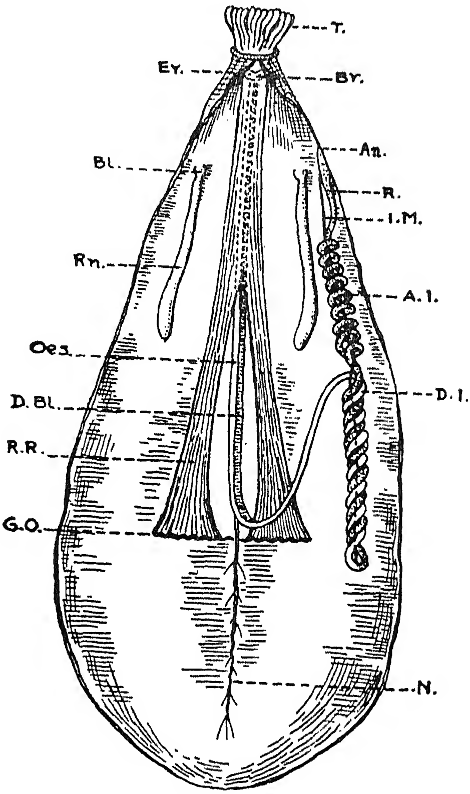
In an aquarium the movements of the tentacles and the introvert are interesting to watch. On account of the unequal contractions of the dorsal and ventral sides of the body-wall, the body assumes a curved form and the animal usually rests on its lateral surface. In this position the anus appears to be on its convex side. If there is sufficient sand at the bottom of the aquarium it bores vertically downwards into the sand with its head foremost. When once completely buried, it may proceed in any direction, either upwards, downwards or sideways. In thus concealing itself in the sand and subsequently thrusting out the tentacles just above the surface the movements of the introvert are very rapid and pleasing to watch.

The food of the animal consists of micro-organisms and organic debris which are mixed with the sand. The particles of sand and the organic substances are entangled into the sticky mucus secreted by the tentacular epithelium and are carried towards the mouth by the beating of the cilia lining the oral surface of the tentacles. When the introvert retracts these particles pass into the alimentary canal mixed with some water. A careful examination of the contents of the intestine shows that the food includes some protozoa (such as ciliates and foraminifera), small flat worms (turbellaria), tiny crustacea (copepods, etc.), polychate larvae and other minute animals.

GENERAL ANATOMY.

The general arrangement of the internal organs is well seen by opening the animal along the mid-dorsal line and turning back and pinning the two flaps of the skin sidewise. On cutting its body-wall an extensive and undivided coelom is opened and a quantity of a pinkish coelomic fluid flows through the incision. The prominent structures seen inside the body are the two ventral retractor muscles (Fig. 3 R. R.), which extend from the anterior end of the animal to two-thirds the length of the body posteriorly. In their anterior half these

muscles form a sort of a tube by the fusion of their margins, while posteriorly they are separate and wide apart. At their origin they are broad, flattened and fan-shaped.



Text Fig. 3. Dissection of Dendrostoma signifer cut open along the mid-dorsal line to show the anatomy. A. I. = Ascending intestine; An = Position of anus; Bl.=Bladder; Br.=Brain; D. Bl.=Dorsal blood vessel; D. I=Descending intestine; Ey=Eye; G. O.=Genital ridge; I. M.=Spindle muscle; N.=Nerve cord; Oes.=Oesophagus; R.—Rectum; R.=Retractor muscle; Rn.=Brown tube; T.=Tentacle. X. 5.

Inside the tube formed by the retractor muscles, is situated the first one-third of the oesophagus (Fig. 3. Oes), which comes to view as these muscles separate and continues back up to their origin. It then bends upon itself and reaches up to the mid-region of the body. The oesophageal region ends here and the intestine begins. The intestine consists of a twisted loop of descending and ascending limbs and of a short coiled continuation of the latter in front of the junction of the oesophagus with the intestine (Fig. 3. D. I. A. I.). The ascending intestine leads into the short straight rectum (Fig. 3. R.), which opens to the outside through the anus (Fig. 3 An.). The

whole of the intestine is wound in the manner of a spiral around a muscle called the "Spindle muscle" (Fig 3. I. M.). The latter extends from the posterior end of the intestinal loop to the anus. The alimentary canal is connected with the body-wall at its oral and anal ends. Thus the posterior half of the oesophagus and the whole of the intestine appear to be hanging freely in the body cavity, particularly the cæcum-like twisted intestinal loop.

Of the vascular system of the animal, only its dorsal blood-vessel or the tubular heart (Fig. 3, D. Bl.) is seen like the oesophagus in its posterior half. It extends from the region of the collar to the origin of the retractor muscles and is in close contact with the oesophagus on its dorsal aspect.

The two brownish-yellow tubular structures situated on either side of the mid-ventral line are the nephridia of the animal (Fig. 3. Rn.). They are also known as the "Brown Tubes". The size and shape of these tubes vary a little in different individuals.

The bilobed brain (Fig. 3. Br.) is situated on the dorsal side of the oesophagus just behind the collar and is covered by the retractor muscles. Each lobe of the brain has at its antero-lateral corner, a black spot called the "sensory pit" or the eye (Fig. 3. Ey.). The nerve cord (Fig. 3. N.) running along the mid-ventral line extends from the anterior to the posterior end and is visible behind the origin of the retractor muscles.

The gonad, whether in male or female, appears as a transverse cellular ridge at the origin of the retractor muscles from the body-wall, (Fig. 3. G. O). The reproductive cells—ova or spermatozoa—are developed on the genital ridge and after liberation are found floating in the coelomic fluid, often in great number.

THE BODY-WALL.

Four layers may be recognised in the body-wall. Beginning from outside they are—the cuticle, the epidermis, the muscular layer and the peritoneum.

The Cuticle :—The cuticle secreted by the epidermis is comparatively thick and tough and affords protection to the animal. It is thick in the trunk and thin and shining in the introvert. Under higher magnifications the quadrate areas of the cuticle appear to be really rhomboidal and to be due to the arrangement of the bundles of the circular and longitudinal muscle fibres inside the epidermis. The whole of the cuticular layer could be separated from the underlying cellular layers by boiling the animal in 1% solution of potash.

The Epidermis :– Next to the cuticle is the epidermis consisting of a single layer of cells, but these differ in size and shape in different regions of the body. The oral surface of the tentacles is lined by columner ciliated cells. The aboral surface of the tentacles and of the collar is lined by cubical and nonciliated cells. Pigment granules of dark-brown colour are seen arranged in the outer half of every cell of the aboral surface.

On other parts of the body the epidermal cells are uniformly more or less conical or pear-shaped with their broader ends abutting against the cuticle (Plate II, Fig. 2, 3 Ep.). They appear to be closely packed in the surface view. Their inner pointed ends which are quite separate from one another lie in a mass of coagulum. The cytoplasm of each cell is full of yellow pigment granules and the relatively large nucleus lies nearer its broader end.

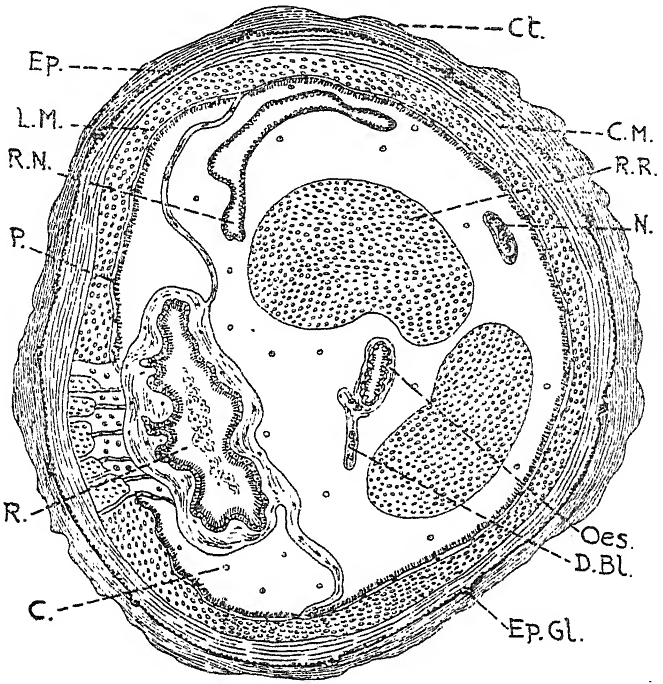
The Epidermal Organs :—The epidermal organs are glandular bodies situated inside the papillæ already mentioned in connection with the external characters. They are of two kinds and are distinguished by the presence or absence of the ducts leading from them to the outside through the cuticle. They are (1) the "Multicellular Glands" or glands without ducts, and (2) the "Sense-papillæ" or glands with ducts.

The Multicellular Glands :—These glands (Plate II, Fig. 2) are more or less restricted to the anterior region of the animal though they are not totally absent from the posterior part. Each of these consists of about fifteen to twenty glandular cells scattered in a trough-like space filled with a coagulum and situated between the epidermis and the circular layer of muscle fibres. Each cell is more or less pear-shaped with a granular cytoplasm and a nucleus at its broader end.

The Sense-papillæ :—The sense papillæ (Plate II. Fig. 3) are seen scattered all over the surface of the body. Each of these is made up of about ten to fifteen glandular cells which are so arranged as to give the glandular papilla a pyramidal form. The glandular cell is drawn out into two processes one at each end. The process at its inner end is thin and hairlike (Plate II, Fig. 3 R.) and is connected with the subepidermal nerve plexus of the body-wall to be described later. The tapering outer ends of these cells are produced into tubules which join at the apex of the papilla to form a minute duct (Plate II, Fig. 3. Ct. D.) which penetrating the thick cuticular layer opens to the outside at the epidermal pore. The whole mass of glandular cells appears to be suspended into the coagulum from the apex of the raised conical epidermis.

The coagulum referred to above is thin and watery in a living animal and is probably secreted both by the epidermis and the epidermal organs.

The Muscular Layer :—As usual the body-wall is mainly made up of an outer circular and an inner longitudinal layer of muscle fibres.



Text Fig. 4. Transverse Section of the animal at the anterior end passing through the oesophagus and the rectum. C.=Coelomic corpuscle ; C. M. =Circular muscular layer ; Ct.=Cuticle ; D. Bl.=Dorsal blood vessel ; Ep.=Epidermis ; Ep. Gl.=Epidermal gland ; L. M.=Longitudinal muscular layer ; N. = Nerve cord ; Oes. = Oesophagus ; P. = Peritoneum ; R. R. = Retractor muscle. X 70.

These muscular layers are not of the same thickness throughout but are thicker in the posterior region of the body making the body-wall appear thick in that part. The muscle fibres are similar to those described by Shipley[1], in Phymosoma varians. The circular or transverse layer of muscles (Fig. 4. C. M.) is thin but thickened round the anus to form a sphincter. The longitudinal layer (Fig. 4. L. M.) is comparatively thick and forms a continuous uniform sheath. Inserted round the rectum are found a number of radically arranged fibres

1 Shipley A. E (1890) On Phymosoma varians. Quarterly J. Micr, Sci. Vol. 31, p. 1.

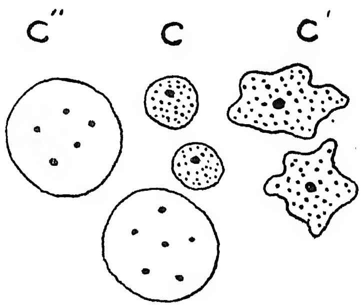
derived from the longitudinal layer of muscle fibres. Their action seems to be opposite to that of the anal sphincter. The fibres of the longitudinal muscular layer are found to be continuous with those of the retractor muscles and as the fibres of both are similar in their histological details, the retractors should be regarded as the separated and the specialized parts of the longitudinal muscular layer.

Besides these there is a short layer of oblique muscle fibres in the body-wall at the level of the insertion of the two retractor muscles.

The Peritoneal Layer :—Inside the longitudinal muscular layer there is a thin peritoneal membrane consisting of a single layer of flattened ciliated cells (Fig. 4. P). It is continued as an external covering to the viscera, on some of which it is not ciliated.

THE CŒLOMIC FLUID

The cœlomic fluid filling the spacious body-cavity consists of a colourless plasma and numerous coloured and colourless corpuscles. It is slightly viscous and coagulable. In the process of clotting there is no formation of the fibrin fibres but the plasma simply separates into a thin serum like liquid and a thick jelly, holding together groups of cœlomic corpuscles.



Text Fig. 5. The cœlomic corpuscles. C. = The coloured corpuscle ; C′. = The amœboid corpuscles ; C″. = The giant cell.

The Corpuscles :—The most numerous are the coloured corpuscles (Fig. 5.) which give a madder-red colour to the cœlomic fluid. They contain a pigment called the "hæmerythrin". The tests employed by Marian[1], in the case of Phascolosoma were applied and the pigment found to be identical with the hæmerythrin found in the cœlomic fluid of sipunculoids like the species of Sipunculus Phascolosoma, Phymosoma and also that of the polychaete Magelona[2]. The corpuscles are discoid in shape measuring 8 μ to 12 μ in dia-

1. Marian G. F. 1927. A note on Hæmerythrin, British Journal of Expt. Biology, Vol. IV, p. 357.

2 Benham, Quart. J. Micr. Sci. XXXIX. 1896, p. 1.

meter. The nucleus is eccentric in position. They are highly elastic like the red blood corpuscles of a vertebrate. They are more or less transparent, homogeneous, refractive when fresh, and appear slightly yellow when examined singly.

The colourless corpuscles are of two kinds, viz., the amœboid corpuscles and the "giant cells". The amœboid corpuscles (Fig. 5. C′.) are nucleated granular cells larger than the coloured ones. Their diameter varies from 12μ to 15μ. They occur in less number than the coloured corpuscles. The second type of colourless corpuscles have been described by Andrews[1] as the "giant cells", from their size and thickness (Fig. 5. C″). They have the same shape as the coloured corpuscles but differ from the latter in being multinucleated and comparatively very large. Their nuclei are three to seven and are situated along the surface. The outermost layer of the cytolplasm appears to be relatively thick and forms a kind of an enveloping membrane. They are fewer than the amœboid corpuscles.

Setna[2] (1931) records a new genus of a Gregarine, viz., Extremocytis dendrostomi occurring in the cœlomic fluid of the Dendrostoma signifer collected from Port Blair, Andamans. Although a number of specimens were examined by us the protozaon parasite referred to above has not so far been encountered in the cœlomic fluid of the Dendrostoma from Bombay.

THE DIGESTIVE SYSTEM

The digestive system is in many respects similar to that of Sipunculus (Andrews, *ibid.*) and Phymosoma (Shipley, *ibid.*). There are, however, a few important differences. The principal divisions of the alimentary canal have been already described in connection with the general anatomy of this animal. The anterior end of the oesophagus is usually distinguished as the pharynx, although there is no morphological difference between it and the remaining portion of the oesophagus.

Microscopically examined the alimentary canal is seen to be covered externally by the peritoneum which has patches of ciliated cells here and there. The muscular layer of its wall is formed by muscle fibres and connective tissue strands loosely intertwined. The internal lining consists of a single layer of columnar ciliated cells, their nuclei being situated near the bases. The intermal lining of the

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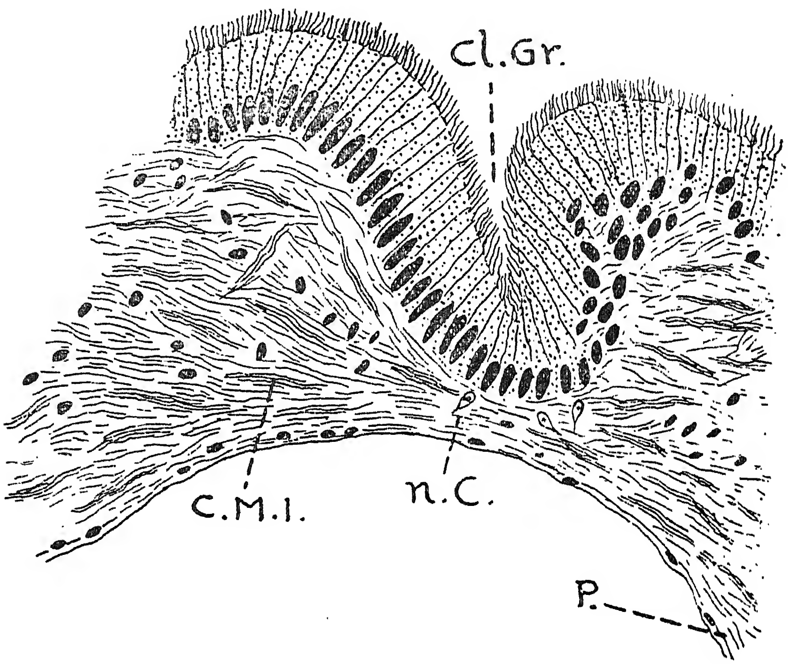
1. Andrews E. A. (1887) Notes on the anatomy of Sipunculus gouldii pourtalis, Stud. Biol. Labor., John Hopkins Univ. Baltimore, Volume 4.
2. S. B. Setna, (1931) Records of the Indian Museum, Calcutta, Vol. XXXIII, Part II, p. 206.

ascending limb of the intestine is folded to form a narrow ciliated groove (Fig. 6. Cl. Gr.) This groove is confined to that part of the spiral which is next to the spindle muscle. A similar groove has been described by Keferstein[1] in Sipunculus.



Text Fig. 6. A horizontal section of the ascending limb of the intestine showing the ciliated groove. C. M. I.—Circular layer of muscles of the intestine; Cl. Gr.—Ciliated groove; N. C.—Nerve cell; P.—Peritoneal layer. X 750.

The Crypts :—The Crypts (Text Fig. 7) are microscopical shallow pits irregularly distributed on the surface of the wall of the intestine and the posterior half of the oesophagus. They are 3μ to 5μ in diameter. Each is surrounded by four or five rows of ovoid glandular cells. The flat bottom of such a crypt is separated by a very thin muscular layer from the internal epithelium. Thus, these depressions appear to be the weak spots on the alimentary canal at which the diffusion of the digested food into the cœlomic fluid may be taking place.

In the mouth of some of the crypts are seen cœlomic corpuscles. (Fig. 7. C.). These crypts differ from the "pseudostomata" of

1. Keferstein W. Beitrag zur anatomischen und systematischen Kenntniss der Sipunculiden. Zeit. f. Wiss Zool. 15. 1865.

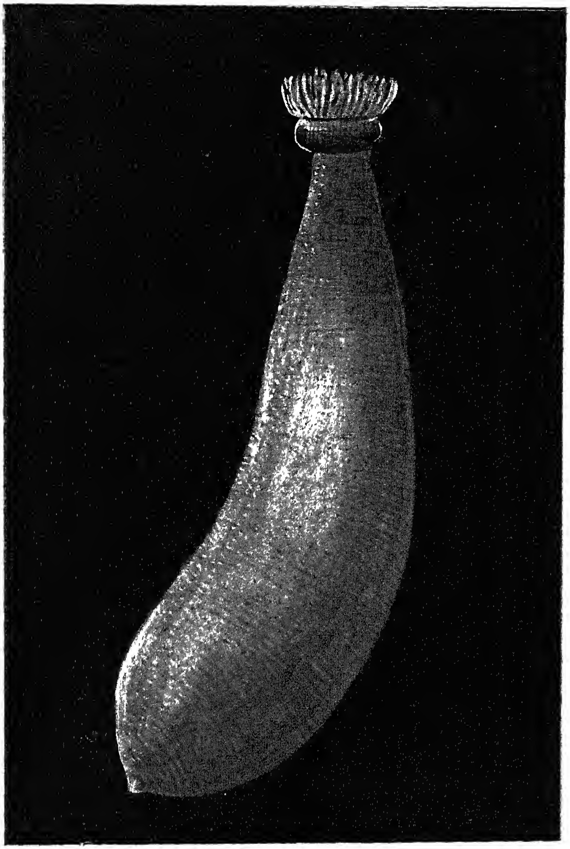


Fig. 1. Plate. I. Dendrostoma signifer Sel et De Man, X 3.
Mth=Mouth.

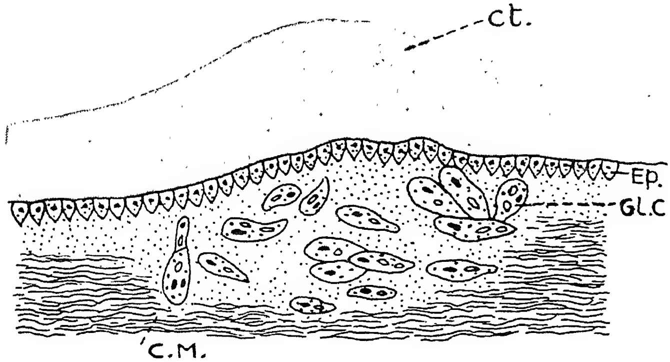


Plate 2 Fig. 2. Epidermal organ (Multicellular gland) as seen in the transverse section of the body-wall. G. M.=Circular muscular layer; Ct.=Cuticle; Ep.=Epidermis; Gl. C.=Glandular cell. X 400.

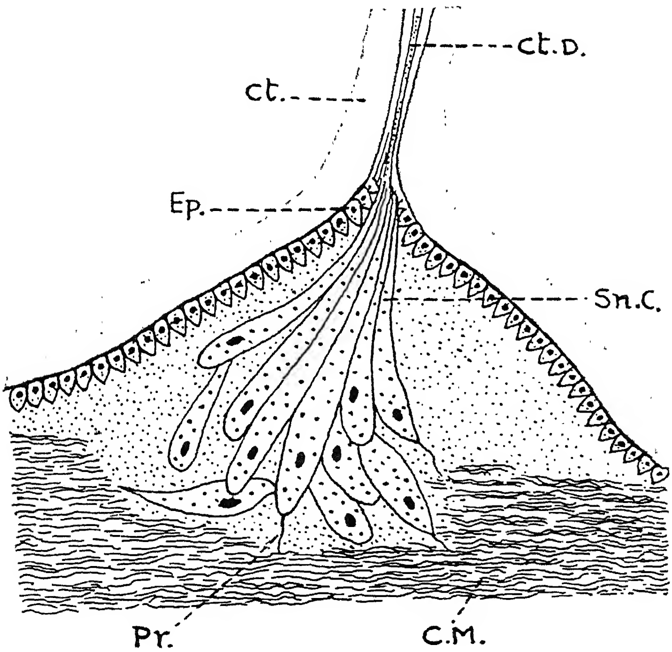
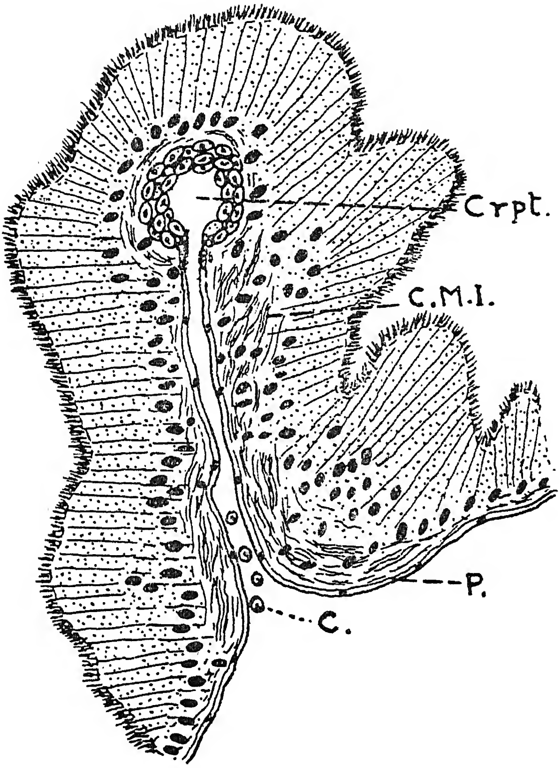


Plate 2 Fig. 3. Epidermal organ (Sense-papilla) as seen in transverse section of the bodywall. C. M.=Circular muscular layer; Ct.=Cuticle; Ct. D.=Duct from the epidermal organ opening to the outside through the cuticle; Ep.=Epidermis; Pr.=Sensory process. Sn. C.=Sensory cell. X 400.

Sipunculus gouldii pourtalis described by Andrews, in being not ciliated and in having depressions from the outside.



Text Fig. 7. Horizontal section passing through the "crypt", on the wall of the intestine showing the crypt opening into the body-cavity, C. M. I. =Circular layer of muscles of the intestine ; Crypt=Crypt ; P.=Peritoneum.

EXPERIMENTS IN ELECTRO-GARDENING.

(with 6 illustrations)

By

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(*Received on April 10, 1935*)

CONTENTS :—Introduction—The Method—Reactions and Results —Mitogenetic or Gurwitsch Rays and Onion Interculture—Theoretical Considerations—References—Explanation of illustrations.

INTRODUCTION.

Preliminary tests with a wide variety of seeds, crops and plants (I) which had been subjected to different electrocultural treatments had shown the pre-eminence of one kind of treatment or of one method. The different treatments employed had been :—

I. Exposure of seed to *Violet Rays* ;

II. Exposure to *High Tension* Electric Sparks ;

III. Exposure to soft X-Rays ;

IV. Sowing, germination and growth in *Radiomagnetic Bed.*

V. Exposure to Ultra-Violet Rays ;

VI. Application of *Mitogenetic* or *Gurwitsch* Rays ; and

VII. *Control* or no treatment for comparison under identical conditions.

The most successful and efficacious methods turned out to be III and IV, *i.e.*, X-Rays and Radiomagnetic Bed (2) in regard to germination and growth and IV, Radiomagnetic Bed, in regard to yield. No. VI was applied separately and in special cases and will be considered by itself. (3).

THE METHOD

Now this optimal method, called the *Radiomagnetic* can be described as follows :—A radio or wireless antenna for capturing atmospheric electricity and magnetism is connected with a bed of iron-wire-netting which captures and concentrates the magnetism of the earth. This bed is laid in the plot to be sown with seed at a depth of six inches so forming a *radiomagnetic* bed. The effect is dis-

tinctly magnetic as previous tests (4) have shown that 20 fruiting shoots of a strawberry plant enclosed in a horse-shoe magnet responded very much more quickly than the fruits on the remaining control shoots of the same plant and gave very much bigger, brighter and earlier ripening fruit. For growing plants and standing trees the method is quite simply modified as follows: If we cannot take our iron wire-netting below their roots we can, nevertheless, take it as close to them as possible, enveloping their roots and stalks or trunks, and, if need be, treat their individual branches in the same way. Hence *jackets, aprons and collars* of iron wire-netting have been made to fit the plant or branch treated as closely as possible, so that the *jacket* or *apron* could reach the roots below and enclose the stalk or trunk and the *collar* the branch as tightly as possible. About 6 inches underground and the same height overground should suffice. But the essential conditions are :—

1. The contact with the root or stalk or trunk or branch should be as intimate as possible ;

2. No damage should be done to the part enclosed in the process, care being taken to replace the earth exactly as it was before.

3. The mesh of the iron wire-netting should not be too narrow, so as to interfere with the movement of air, water, etc. in and round the roots of the plant.

4. Thereafter such *ulterior* treatment should be given, if necessary, as :—

(*a*) Sparking the wire-netting ; or

(*b*) Connecting it with an aerial.

The stage and modality of this *ulterior* treatment is fixed by very careful observations from day to day and indeed from hour to hour of the same day. Thus, if the improvement caused by the radiomagnetic *jacket* or *collar* tends to peter out after having reached a maximum which of course is determined by a comparison with the controls, then a high tension discharge for a minute or two is advisable. This is done by means of a small induction coil, fed by a six volt battery of, say, a motor car lighting out at a distance of 25 millimetres for sparkgap corresponding to 1,250 volts of the spark playing on to the *jacket* or *collar*. If, again, the plant or the soil or the sub-soil tends to be infested with white-ants or other insects such sparking will kill or drive off all the pest. The current consumed is infinitesimal, due to the very brief duration of sparking, 20 plants taking 0·01 unit only.

5. Generally, the more moderate the treatment, the more effective the results.

This simple technique can be varied to suit individual needs but will be found dependable in the large majority of cases.

REACTIONS AND RESULTS

Continued observations from day to day have shown a definite response in every case. The usual form or forms which such response has taken have been very easily noticeable when the treated or energised and the control or untreated plants are kept side by side or as close together as possible. In the case of big standing fruit trees obviously care has to be taken in the choice of treated and untreated trees so as to keep in their case every other factor identical except that of the treatment. The response given to the treatment falls under some or all of the following heads :—

1. The treated plant or tree has a healthier and brighter look than the control.

2. The leaves appear greener, fresher and straighter than those of the control and they are with no leaf-curl, which mark the control.

3. The growth is accelerated all round ; leaves get denser and more new leaves are formed ; new shoots begin to appear ; inflorescence or flowering is more rapid ; and bigger and better fruit is formed.

4. Resistance to plant disease is very marked : the control looks a defective, degenerate and backward plant in comparison.

5. The normal growth in the life cycle of the plant or tree may be accelerated by weeks and even months, without any observable damage at any stage.

No.	Name.	Farm.	Object.	Treatment.	Response	Remarks.
I.	Sweet lime.	Agaskar, Bombay.	Better growth	Seedlings prepared from seeds of 'Mosumbee' (sweet lime) obtained from Zanzibar were subjected to onion interculture tests.	Those with three onions each planted at a distance of 1·75 inches from the stem died. Those with two onions at the same distance showed a growth of one-sixteenth of an inch on a total height of 1·25" over the control in a period of a week; and those with one onion showed no difference.	Onion interculture is a very powerful means of administering Ultraviolet Rays direct to the roots of the tender seedling. The limits of inefficacy, efficacy and super-efficacy or death lie very close together. This amply confirms the results of tests with Ultraviolet Rays obtained not biologically but physically.
	Sour lime.	do.	Better growth	Onion interculture.	3 years old plants show superior growth over the control; in a fortnight measured 2".	The three year old plant is naturally more resistant, takes stronger doses of Ultraviolet rays administered as above, than the small seedlings which are very delicate and for which even mild doses prove lethal.
	Cauliflower, cabbage & Kohl-Rabi	do.	Better growth	do.		Cauliflower had more profuse foliage, but formed no flower *compared with control.* Cabbage and Kohl-Rabi have responded to the treatment, size & quality being better than untreated plants.

No.	Name.	Farm.	Object.	Treatment.	Response.	Remarks.
	2 Chikhoo plants.	Agaskar, Bombay.	Better growth	Radiomagnetic treatment.	A powerful response was detected. The plant which used to flower sparingly now flowered profusely & showed full bloom but here again the flower did not go into fruit and dropped off. The backward plant showed vigorous foliage and produced fruits which were certainly very much larger than it ever produced before. The form which lost its flowers continues very vigorous with beautiful foliage.	Vegetative growth is invariably fostered by such treatment.
	Hibiscus, Rose.	do.	Better growth	do.	Hibiscus showed a decided improvement. The foliage is beautifully healthy, green & the flowers are certainly very much larger than ever before. It had been under observations for several years but never before had it yielded such big flowers. Other varieties of Hibiscus plants grow-	It confirms the behaviour of a very large majority of flower plants under the Radiomagnetic treatment.

					ing in the garden which were not subjected to any treatment but kept as control have had foliage & flowers exactly as usual in the past few years. Roses have certainly improved under treatment which in itself is remarkable as roses do not normally thrive by the seaside.	
II.	Rose plants	Collector's garden, Mainpuri	Better growth	Radiomagnetic treatment.	Response noteworthy.	
	Sun flower	do.	Better growth	do.	Brighter colour of the flower. Vigorous budding and flowering & longer life of the flower and the plant.	
	Mango.	do.	Better growth	do.	Response has been more prompt and definite.	
III.	Sugarcane.	Siddhu Mainpuri Experimental garden	Better growth	Electric sparking.	Mealy-wing insects were killed.	Pink bollworm, white-ants, aphis and a variety of insects have been killed.

No.	Name.	Farm.	Object.	Treatment.	Response	Remarks.
	Kachnar	do.	Better growth	Radiomagnetic treatment.	The treated plant began to throw out leaves and buds. The vegetation of the treated plants is decidedly more healthy than that of the untreated ones. One branch of the treated plant was further treated branch to branch and the next kept as control. No change was seen. The response of the treated tree is normal and accords with expectations but the behaviour of the branch treated is unresponsive.	
	Mulberry	do.	Better growth	do.	It has budded and is in advanced stage of growth.	Mulberry response is in confirmation of previous experience vide Bulletin "*Growing Fruit with Electricity*" 1934, p. 3.
	Cocoanut	do.	do.	do.	Plants that were dying began to revive and after another 2 weeks began to put out shoot.	

	Chandni (white-flower plant)	do.	do.		Improved in colour of the plant which went from pale green to deep green.	
IV.	Santras	Rang Bahadur Mainpuri garden.	do.	Onion interculture.	Santras, not fruiting, growth stunted, were treated and improved in vegetative growth and threw out shoots. Others treated with *jacket* and Onion Interculture showed very good vegetative growth. Still others which had crumpled and fained fruit which would not ripen but fall off gave a rapid response to treatment and improved in shape and are ripening on plant.	
V.	Guava ratoon-plant.	do.	do.	Radiomagnetic treatment.	Showed marked improvement in growth.	
	Mango Langras.	do.	do.	do.	Flowered profusely.	
VI.	Var. Mohanbogh.	Brijlal Gursaiganj Papaya farm	do.	do.	Improved 50%.	These varieties of mango do well.

No.	Name.	Farm.	Object.	Treatment.	Response.	Remarks.
	Var. Mathena Rampur	Brijlal Gursaiganj Papaya farm	Better growth	Onion interculture.	New buds came out. General condition healthy.	
	Var. Dajai Bhagalpur.	do.	do.	Radiomagnetic treatment.	Disease arrested, buds coming out, fresh growth.	
	Var. Amman Ibrahampur	do.	do.	do.	Fresh growth started, slight improvement.	
	Papaya Var. Phillipina	do.	do.	do.	Very good fruit-setting.	
	Papaya Var. honey-dew	do.	do.	do.	Fruit setting begins.	
	Var. Kalwa Chaulpa	do.	do.	do.	Improved wonderfully.	
	Grapes Bhakri	do.	do.	do.	Plants are giving out new buds, slight improvement.	
	Fig.	do.	do.	do.	Slightly improved.	

	Kathal (Jack fruit) Khwaja Dhar-bhanga.	do.	do.	do.	General condition healthy, throwing out new leaves, poor growth improved.
VII.	Roseplant.	Kichlu Garden Allahabad	do.	do.	Fresh and healthy, put out new leaves & shoots on bare twigs. Improved all round.
	Papaya.	do.	do.	do.	Leaves healthier, straighter & green.
	Hibiscus	do.	do.	do.	Rapid formation of shoots and buds.
	Brinjals & Kachals	do.	do.	do.	Improved all round.
VIII.	Chillies (4 sets 4 exhibits from 4 farms.)	Electro-culture section Mainpuri-Rural uplift Exhibition	do.	do.	Early and more profuse flowering ; healthier & bigger.
	Brinjals (2 sets 2 exhibits from 2 farms.	do.	do.	do.	Treated plant is healthier and has bigger flowers; control is smaller and has not even flowered.

No.	Name.	Farm.	Object.	Treatment.	Response.	Remarks.
	Knol-Khol	Electro-culture section Mainpuri-Rural uplift Exhibition	Better growth	Radiomagnetic treatment.	Treated plant is six times the control.	
	Rasp-berries	do.	do.	do.	Treated plant shows better growth and bears many fruits; control smaller and has only a few fruits.	
	Bitter gourd.	do.	do.	do.	Treated plant 7 times the control and budding early.	
	Tomatoes	do.	do.	do.	Treated plant bears big fruits.	
	Cabbage (2 sets, 2 exhibits from 2 farms)	do.	do.	do.	Treated $1\frac{1}{2}$ times the control in size.	
	Roses	Mr. Siaram's Rose flowers	do.	do.	Bears big flowers, profuse and healthy.	
IX.	Aonla (Phillanthius Emblica)	Bishen Mansing Fatehpur garden.	do.	do.	Grew in 4 months from 3 to 9 ft. in height, thickening & widening in proportion.	It may be objected that isolated trees do not furnish enough material for scrutiny, but it must be remembered that with fruit trees in a grove or garden where variety is the rule, the case is not the same as with a corn field which

						has thousands of plants growing. Further it is only the backward diseased or otherwise affected trees which are naturally subjected to treatment as the healthy ones call for no special handling at all and hence the individual behaviour of such backward diseased or otherwise affected trees must be studied with special care. In the above instances results are not declared at once and the impatient enthusiast anxious to register response could easily have given up the treatment as failure but the long wait of eight months proved beneficial to show that everywhere no outwardly visible results declare themselves. It by no means follows that the treatment given has been ineffective. Now the falling of flowers before fruiting is a sign of vigour into vegetative growth which has been confirmed in the course of our experimentations vide the first tests on mangoes. This further proves that the behaviour of a plant under the Sparking treatment as in the case of orange and under the Radiomagnetic treatment above is alike. Also special measures will have to be taken to stop the inrush of the energy into vegetative growth and secure fruiting proper. A solution of this very important problem is being attempted elsewhere.
X.	Miscellaneous :- Pomegranate, guava, falsa	Fatehpur Collector's garden.	Better growth.	Radio - magnetic treatment has been standardised to comprise *jacketing* at roots or *collar*	Response has been uniformly positive, increased growth, or accelerated shooting, leafing, fruiting etc. A typical and stri-	

No.	Name.	Farm.	Object.	Treatment.	Response.	Remarks.
	(Grewia asiatisca) mulberry, gular (Ficus gomerata), custard-apple, mahua (Bassia latifolia), grape-vine, plantain &c.		Better growth	on the stem or branch with or without Sparking at 1,250 volts for 2 minutes if *ulterior* treatment is needed.	king case is furnished by mahua which due to treatment flowered 20 days earlier and gave double the weight of flower (40 as against 20 seers).	

Encouraged by these results very elaborate tests have been undertaken in Sicily where certain plantations are affected with a sort of dry-rot called "*malsecco*." The writer visited some of the worst centres by invitation. This is widespread in the East and going by superficial symptoms. There is reason to think that it is prevalent in India as well. Tests have been begun in Italy under the writer's guidance and reports are coming in by Air Mail. A preliminary report has been published (5).

MITOGENETIC OR GURWITSCH RAYS AND ONION INTERCULTURE.

Previous tests had shown ultraviolet rays (6) to be very effective if applied in very short doses and a practical application of the same has been through the biological agency of the so-called *Mitogenetic* or *Gurwitsch Rays* (7). Gurwitsch has shown onion roots are very rich in such rays, which are comparable with mild ultraviolet rays being of the same order and here we have found the response to such rays emitted by carrots and castor as well from a variety of chillies (Capsicum frutescens), linseed, lady's finger (Hibiscus esculentis) etc. Advantage has now been taken of the onion root which is a powerful emitter of these rays to favour the growth of very backward and sickly plants such as lime and mango, by planting a number of onion plants around the sickly plant and as close to it as possible. This takes one into the big subject of interculture which has to be interpreted from the electrocultural viewpoint, but so far as fruitgrowing is concerned, be it noted here that definite results have been obtained. Thus a very valuable but sickly mango graft plant which was dying was helped to grow by having a series of onion plants sown around it. Similarly, a sickly lime improved with such interculture when all other methods had failed.

THEORETICAL CONSIDERATIONS

It may now be asked what exactly is *the theory* of such treatment and the cause of the improved growth that follows.

Our theory of radiomagnetism according to which minute electromagnetic disturbances including the earth's electricity and magnetism are captured and transmitted to the growing plant has found support from some very recent communications to the First International Congress of Electro-radiobiology. Nadson (8) finds that metals such as Al, Fe, Cu, Ag, Sn, Pt, Au, Ph, retard the germination and growth of white mustard, about to germinate, by distance action at a distance of 2 to 3 mm. His theory is that electrons issue from the metals under the radioactivity of the surrounding air, soil, etc., bombard the organism, retard its growth and even kill it. But such action

has been favourable when (*a*) very little metal in the form of wire-netting is used; (*b*) the distance is safe enough, we have had 6 inches as minimum; (*c*) metal plates are used and the distance is 9 inches as in the case of strawberry plants placed on a metal plate and (*d*) the larger the plant or tree the smaller the *jacket* or *collar* used.

Further support is given by *Rivera* (9) in a similar paper at the same meeting, who has shown that the biological effects may become attenuated and even disappear by covering the metal with a layer of paraffin, or a film of water or nutritive liquid, or a sheet of paper or glass, or a coat of oxide or carbonate and that susceptibility to such distance varies from individual to individual, and from stage to stage of growth. The effects are inhibitory or exciting, according to the greater or lesser susceptibility of the species or tissue. Rivera too postulates ionisation of the air, as the causative factor or the stimulation or the inhibition.

As regards the effect of electric sparking, we have got increased percentual growth, compared with the control, of 30 to 150% during tests lasting several years with nearly a hundred species. Now Riccioni (10) in a paper called the Electric Currents and Biological Manifestations has obtained an increase in wheat ranging from 40-45% to 370-270% due to the effect of varying electric currents acting for very brief periods on seed. To explain the mechanism he proposes the hypothesis that the embryo of the seed during the resting stage contains electric charges in a state of stable equilibrium and the sudden variations after the charges to a new state of sufficiently stable equilibrium favour the latent energy of the seed.

The essential point is that these disturbances must be mild and brief, otherwise more harm than good is done. This has been repeatedly shown by the beneficial effects of *Gurwitch* or *Mitogenetic* rays.

The theory cannot however be developed with perfect accuracy. But there is no reason why the agriculturist and the horticulturist and the orchardist should not take advantage of the latest methods, even if the underlying theory is imperfectly understood.

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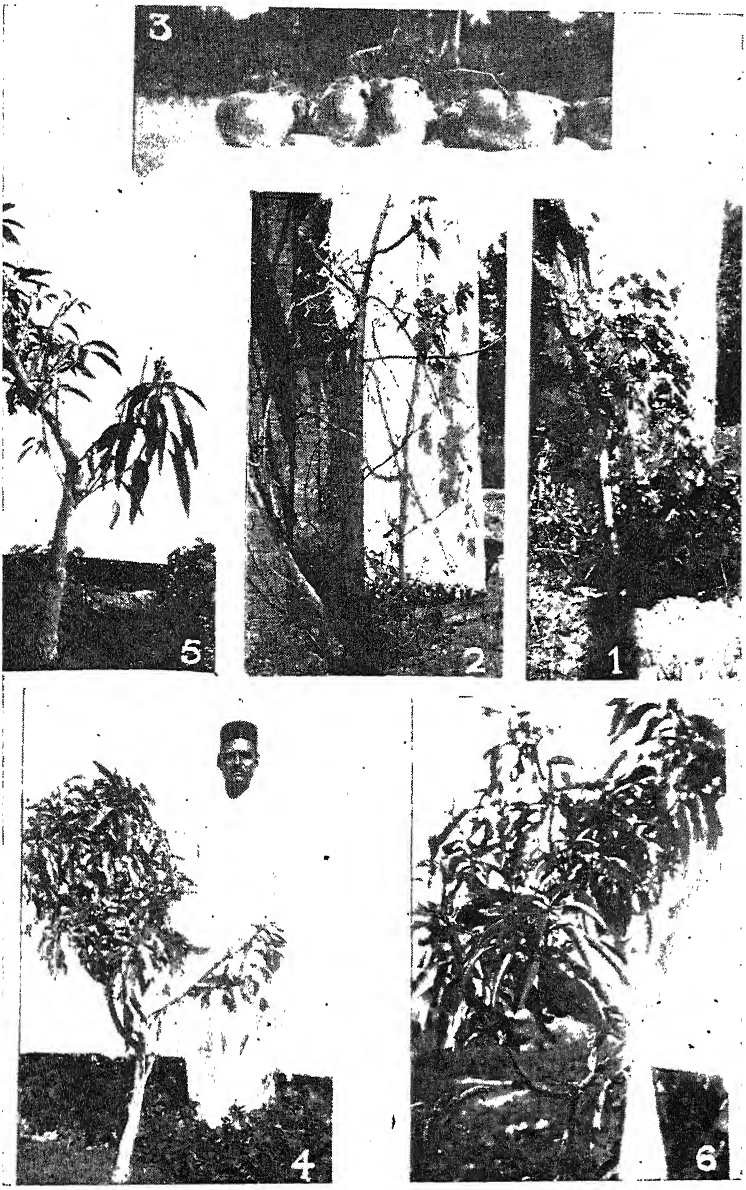

PHOTOGRAPHS

1 & 2 Grape vines. Sixteen plants were treated and control alternating were tested. One pair of adjoining such is shown. Note the dense foliage caused by treatment.

3. Tomatoes. Left row is the fruit of control plant. Middle & right rows show the fruit of treated plant. Increased growth and size of fruit due to treatment is 100%.

4, 5 & 6. Mango grafts. Diseased, defective or dying mango grafts restored to health by treatment. No. 4 is a 4-year old graft which was dying and had only a couple of leaves left. It received new life after treatment which begin in Christmas 1934, No. 5, this plant was dead with not a leaf left and only stem standing, but revived out of recognition. No. 6 was a half dead plant, but revived after treatment. Withered branches

Electricity & Plant Growth (Nehru), Presidential Address to the Indian Science Congress Section of Agriculture, Bombay, 1934.

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(5). *La Gazzetta della Sicilia, 3 febbraio* 1935, p. 4.

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(9). Proceedings of the International Congress of Electroradiobiology, 1934.

(10). Proceedings of the International Congress of Electroradiobiology. 1934.

Note.—Irradiated irrigation tests which were conducted after this paper had gone to press has proved exceptionally successful with seeds, seedlings and plants. This consists in irrigation with water which has been subject to violet rays and High Tension Spark.

THE MICROBIAL ASPECT OF THE PROBLEM OF MANGO PRESERVATION *

By

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I.—INTRODUCTION

The problem of mango preservation has now developed into one of great importance from the point of view of economics, attracting the attention of growers as well as of scientists in our Presidency.

Even in attempts to preserve the fruit for the brief space of time required for the transport of the fruit from the field to the market, considerable losses occur due to various causes. Prominent among these is the deterioration due to the very nature of the fruit (its consistency, etc.), which in its turn facilitates the action of other factors, *e.g.*, the indefatigable energy of the Micro-organisms to seek food for themselves.

In this paper we do not propose to consider the point of its consistency and we leave it to the care and discretion of the Horticulturist and the Plant Breeder. But we have all the same to refer to the mutual relation between texture and microbial action. That the texture of the fruit has to be taken into account becomes evident when we consider that the possibility of an attack of micro-organisms is rendered the more likely, the more delicate the protecting covering is affording the organisms a better chance of finding their way in. It is evident that once they enter it, there can be no talk of fruit-preservation. Our experiments have revealed beyond doubt that the microbial invasion is rendered very difficult, if not impossible, even under very favourable conditions of temperature, if due care is taken to see that the fruit remains unpunctured. This was found to be the case with many other kinds of fruit also.

The only method so far discussed as promising in the preservation of the mango is cold storage. In this connection the results of the work done so far in different parts of India, especially in Poona and Bangalore, could be summarized as follows :

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* We express our thanks to the University of Bombay for having sanctioned a grant towards the expenses of this research.

1. Ripe mangoes plucked from the trees can be kept normally from eight to ten days, after which period they get over-ripe, and fungal and other attacks set in. This is probably due to the ripening enzyme being active on account of the high temperature (30° to 32° C.) prevailing in June and July.

2. The rot usually starts at the place where the stalk is attached to the fruit and then gradually extends to the whole fruit.

3. Paraffining the stalk does not prevent rotting.

4. The rot could be delayed to some extent by keeping the fruit at the temperature of ten degrees centigrade, but could not be effectively stopped.

5. Fully ripened mangoes removed to 10°C. kept well for three weeks, after which time they lost their distinctive colour, and the skin gradually assumed a brownish black tinge. The flavour and the taste were not affected in any way. Another week more and the fruit lost the flavour, being overripe.

6. Fruit partially ripened at the room temperature before being transferred to the ten degrees temperature, kept well for six to seven weeks in appearance and flavour. But thereafter it began to shrink, although there was no rotting except in the case of injured specimens.

7. In the case of raw ones, if stored at ten degrees, ripening was uneven and there was no guarantee of their ripening uniformly.

8. The ripening enzyme or enzymes remain slowly active at the said temperature, provided they are already there. One cannot be certain of their presence in raw mangoes.

9. The enzymes remain active up to a period of three weeks at the above temperature of ten degrees.

Although we followed and repeated these interesting experiments, we do not propose to offer any remarks on them, not being entirely within the scope of our work, beyond saying that No. 2 may not necessarily be the case and that our observations connected with No. 3 will be found later, in this paper.

In view of these results it was not very encouraging to investigate further the problem of mango preservation. But as the Microbial side was not studied in this work the present study was undertaken to fill in the gap.

Before we begin the consideration of the Microbes the previous attempts made to keep off their attacks must be mentioned. The work of Mr. R. S. Kasargode, Asstt. Prof. of Entomology in the Poona Agricultural College has established that the ordinary method of Petrol fumigation with the object of preventing destruction by

microbes does not prove very successful; and that in the case of the Potato, on which he worked, the loss due solely to these agents was estimated to be as much as 55%. Now the Potato has a much tougher consistency than the mango. This might give an idea of the losses to be expected in mango preservation.

The importance of the problem was not realized before, as only recently the export of the fruit has been thought to offer a big promise of opening new avenues for the Indian agriculturist and the fruit grower. The Horticulturist of the Bombay Government lays special stress on the methods of packing, etc., which only supports our plea for the choice of a tougher kind of fruit if success is to be achieved in the attempts to export the mango.

II.—INVESTIGATION OF THE PROBLEM *

Now leaving the points of consistency and proper selection to the Horticulturist, we undertook the present work with a view to bringing under control the microbial action. The investigation was begun in the early part of 1931 and the work done so far strongly suggests that much remains to be done in this matter. The complete study of the microbial spoilage of the marketable mango fruit includes many side-problems and complementary questions. Without neglecting them, or rather, postponing their treatment in detail to a further date, we are justified in concentrating now on by far the most important cause of that spoilage which we call here the *common mango rot.* From what we say later, we could call it the common fruit rot; but we may give it for the time being the name of our most prized Indian fruit produce. Its morphological and taxonomical study may be the subject of another paper. We shall consider now its physiological and bio-chemical characteristics, especially those which may be of importance from the point of view of preservation.

The actual work on this common rot of the market mango was started in the month of June when the fruit was in full swing. The actual variety of fruit, on which we concentrated in our work, without however forgetting others, was the one commonly known as the Malgova. It is a very delicious fruit, green in the rind even when fully ripe, and with all the peculiarities of a highly prized variety. The most noteworthy point is its pulp, which is absolutely free from any fibres or threads. The size of the fruit is not small and the length

* The illustrative tables and graphs which have been abstracted in the body of this paper and a few bibliographical notes may be published in another paper when we close our work with a study of the morphological and taxonomical character of the rot-micro-organism.

from the point where the stalk is attached to the point just opposite is about 6 to 7 inches.

Actually where the fruit is spoiled by the lesion, the whole mass is a little translucent and the skin a little darkened and very easily breakable. The fruit generally gives out from the lesion a watery fluid, and the whole of the pulp at the point is in a loose putrified condition.

For investigation the fruit was cut open aseptically to avoid any more infection from without, and the pulp was examined microscopically to see if any clue could be obtained as to the agent of the spoilage. The pulp was placed on a slide and the whole mass nicely disintegrated with the help of dissecting needles. This examination with ordinary methods of staining revealed certain actinomycetic elements. In order to isolate them we resorted to ordinary and special methods of culture. A number of the Petri dishes with Actinomyces medium were inoculated with a portion of the pulp from the diseased fruit. The dishes were exposed to a temperature of 37°C. After 24 hours they all showed a profuse growth of fungal nature but no bacterial colonies were seen. The controls were found sterile even on the second day. Again to see if the pulp of the fruit was sterile in the natural state, the pulp of a healthy fruit from an unpunctured place was taken and cultured on the same medium in different places. This gave no growth showing that the fruit does not necessarily harbour the disease elements. The fungal elements were transferred to two different culture tubes and one was kept aside as a stock culture. With this it was possible to reproduce the disease with the same symptoms at will in 100% of the cases.

To see whether the fungal attack was peculiar to mango or whether other fruits also were equally subject to its attack, different kinds of them were locally purchased, and the same agent of disease was tried on every one of them. The results are given below. They were all seen to be subject to the action of this disease.

One of us (*Karkare*) personally visited the petty shops of the city and looked for the rotten fruits. The majority of the fruits were found to be infected in a similar manner, especially the more succulent ones like the papaya. Samples were collected and taken to the laboratory. A microscopical examination showed in every case the morphological similarity between the fungal elements found in these fruits and those found in mango. And culture plate experiments and actual inoculations were carried out in their case.

It may be that they all belong to the same parent stock, but a detailed survey of all the cases, in order to trace back the origin of the

contamination was obviously not possible. These complementary experiments were carried out on the following fruits in which special attention was paid to the pH of their juices.

Apple (var. Kashmere and Japan)	with pH	5·2
Plantain (var. Rajali, Welchi)	" "	5·2 ; 4·8
Mango (Totapuri and Malgova)	" "	5·1
Chikoo	" "	5·4
Papaya	" "	5·8
Orange	" "	4·4
Pear	" "	4·2
Lemon	" "	2·4

Other fruits and materials were tried but we consider the foregoing sufficiently representative.

In these experiments the only fruit which withstood the attack pretty well was Lemon (2·4) but even this fruit showed signs of decay on the fourth day. The smaller variety of the plantain also showed a little resistance but not for a long time. All these fruits were injected with a portion of the rotten pulp and all have shown the same signs of rotting.

The fact that fruits of such different kinds and having such widely diverging pH concentrations were attacked, suggested a special experiment to test the behaviour of the rot in question, with various degrees of acidity.

To get a suitable series of pH we prepared the series ranging from 2·2 to 7·4 based on the suggestions of McIlvains.

But before we proceed to examine the tests on these series, we want to record the interesting facts observed in our work which led us to concentrate our attention on the chemical composition and the reaction of the affected plant. While trying the rot on different fruits it was noticed that it flourished better on the skin of Plantain than in the pulp within, quite contrary to expectations.

Further experiments showed that it was not a question of the concentration of oxygen. It was then evident that the sugar content was not quite an essential condition of the disease. It was therefore thought advisable to see the chemical composition of the plantain in order to see if that would give any clue to the food requirements of the rot. In this connexion reference must be made to the very valuable work of *Burns & Joshi* (Agricultural Journal of India, 1920, p. 386), on analysis of fruits. The results of those analyses were especially verified with regard to the sugar contents and the phosphoric acid contents, and having found that our results coincided with those analyses we accepted the other figures as correct.

Another important thing which we noticed in the experiment with all the fruits was that the fungus showed a remarkable preference for the Orange. In this case the fruit was cut open and cultured with the rot in question. The whole was covered with a bell jar, and a container with some water was placed inside. When in experiments on the mango the pulp was examined on a slide, the appearance of the fungus was constantly that of a non-typical form of actinomyces. But this experiment on the Orange proved certainly that this was far from being the case. The rot produced such a profuse growth that the whole of the fruit was shrouded with hyphæ and not even a small portion of it was visible.

Now, since it was seen that the rot invaded the skin of plantain more than the pulp, an experiment was started in which the skin of plantain was nicely separated from the pulp and smashed and sterilized in a Petri dish. This mash of the skin was again inoculated and incubated at 37° C. Within the next 24 hours there was a good growth. As there was no sugar in the skin, it was concluded that there must have been something else in it that either provided the nutrition to the rot organism or made the substances of the skin available. As the analysis showed a good P_2O_5 content, this was first examined.

The skin-mash of the same fruit was extracted with water repeatedly until further extracts gave no more perceptible positive test for phosphates. The whole extract was then treated with calcium hydroxide and thus all the phosphates were removed. Then both the mash and the skin were sterilized and cultured at the same temperature.

As a result of these experiments it was noticed that the culture in the extract did not grow in the period of 24 hours as is usually the case. This indicated that the phosphate may be indispensable. When to the same dish a few drops of a solution of phosphoric acid were added, a good growth was obtained in the same period of 24 hours. However it must be mentioned here that this growth did not occur at a temperature of 37° C. but at room temperature which was about 29° during those 24 hours. To confirm this fact the same set of experiments was repeated and the above effect of the Phosphoric acid was verified.

This would suggest that the action of P_2O_5 was an essential condition for the growth of the fungus. But we made further experiments with cultures in different solutions and the results clearly showed that the Phosphoric acid content was not an essential condition and that it only accelerated the growth of the rot.

Since phosphoric acid had such an effect it was thought worth

while trying other acids of the fruits with the same fungus. The most common acids of the fruits were selected and cultures were made either alone or in combination with carbohydrates. A noteworthy result was the absence of growth on malic acid and an abundant growth on citric acid.

It can be positively said that the rot favours citric acid more than any other acids of the fruits. Now this conclusion is quite in keeping with the results of the chemical examination of Mango which gives 5% of citric acid.

There is no indication of any metallic ions being present in the fruit but it was thought of some interest to see in detail what would be the effect of different metals on the growth of the organism for the purpose of using or avoiding them in the process of preservation.

As the rot had shown a special inclination towards citric acid different salts of the same acid were tried. The work on this point showed that of all the combinations with acids and metals that of magnesium and citric acid served the best. This metal, however, has a general favourable effect on the organism since we found that other salts of the same metal with different acids had the same good effect; although, as we said, there was a marked degree of preference for that combination of magnesium and citric acid. Next to that, came the tartrate, then the carbonate and the sulphate. Scanty activity was shown in the phosphate and still lower in the chloride.

All these observations were made on glucose cultures kept at 37° C. for 96 hours, *i.e.*, 4 days, so that it must be supposed that the effect of the Mg-ions is only temporary and that it only accelerates growth, *i.e.*, its rate, and not the total growth. The experiments mentioned above showed that the total growth was also greater and that after 96 hours—a rather long interval.

Now while working on different media, we could see that there was always a better growth whenever glycerine was a component of the medium. This suggested the idea that the organism might convert the carbohydrates into glycerine before assimilation. The yeasts of certain species have a remarkable power of producing glycerine and under certain circumstances they are known to yield as much as 33% of glycerine. To ascertain whether any similar effect in the case of our organism is produced, experiments were started. But at the outset we have to state very carefully the problem. The fact that the organism uses glycerine for growth is by no means a guarantee that the same is produced by it. The acrolin test was applied in our case and gave negative results. However, one thing we know

is that, in the presence of alkaline salts, fructose is produced from glucose and our experiment has shown that in the presence of Magnesium salts a glucose culture will grow better than a culture either only of glucose or only of fructose.

This observation raises the question whether the organism's growth is a function of the magnesium present or whether the presence of the salt converts the glucose into fructose which is then utilised by the organism. But this latter suggestion is not likely to be acceptable in view of the fact that a culture in fructose alone does now grow as well as it would do in a mixed medium of Mg. salt and glucose. There still remains the possibility of some glycerine being produced, but if so, it must be immediately utilised. It is the province of the biochemist to answer the last problem.

It may be interesting to note that the alcoholic nature of glycerol has apparently no influence on the growth, since it was seen that mannitol cultures, under the same conditions of glycerol culture, did not thrive well, and while the glycerol culture showed a massive and uniform growth the other was scanty and not quite homogeneous.

From the stand-point of Hydrogen ion concentration and its effect on the micro-organism, its wide tolerance was very interesting. To study its growth, in an accurately calibrated series of pH tubes we put mixtures with different pH with an interval of 0·2. Of course, the experiments on the growth of the organisms on different fruits of divergent pH values strongly indicated its capacity for adaptation to various conditions and the trend of the results to be expected 'in vitro'. The power of the organism of utilizing citric acid and the fact that phosphoric acid favours its growth were taken advantage of in selecting a proper series of mixtures. McIlvains pH standard mixtures composed of solution of Sod. Hyd. phosphate and citric acid (Clark, p. 116) served the purpose quite well and were used as the growing media. The series selected was from 2·4 (pH of Lemon) to 7·4 (a little higher than the point of neutrality). Once incubated it was seen that the whole series showed good growth, making it quite clear that the varying concentration of these H ions had no appreciable effect on actual growth and that the idea of preventing the disease by surrounding the fruit with a substance of a suitable pH value would simply not work. The tubes in the above experiment were exposed to the room temperature which was about 29° C. This was thought necessary on account of the presence of the phosphoric acid in the mixture of control tubes ; as our previous experiments had shown that with phosphoric acid the rot fungus did not grow at 37° C, but at room temperature in 24 hours.

Malic acid, it may be noted here, is not used at all as indicated by the absence of the fungus growth although its pH value is 2·4, whether the culture is exposed to room temperature or kept at 37° C.

From these and other repeated experiments we can generally say that as the point of neutrality is reached the growth seems to weaken although it persists; and secondly that the tubes of the pH values 3·6, 4·6, 4·8, 5·4, 6·6 and 6·8 show a meagre growth indicating an optimum pH varying with cultural conditions between 2·4 and 3·4.

As regards the different sugars, it was seen that there was nothing like a preference for any one of them except perhaps in the case of lactose, where there was a little better growth than in the rest of them. It may be said here that although there is no difference of growth among the sugars themselves, it is enough to add a magnesium salt to any of them to obtain in it a conspicuously favourable growth.

It remained to be seen whether the disease mould would grow in anaerobic conditions and for this purpose, plates with actinomyces medium were cultured and placed in a desiccator connected to a 'Genco' exhaust pump. The conditions were kept anaerobic for 96 hours and it was seen that the rot-mould did not grow on the plate. Here of course there was the possible conclusion that the medium had been rendered unavailable due to the moisture having been also exhausted by the pump. So a second experiment was arranged in which a dish of water was placed inside the desiccator. The medium was, of course, the same with the same acidity (pH 6·0); the error of the previous experiment was thus eliminated and the result was that the culture did not grow so well as before. This would suggest that the growth of the fungus is checked appreciably, if not retarded altogether, by anaerobic conditions.

The above experiment was made with an artificial medium. We now thought desirable to see what would happen if the real fruit was subjected to the same experimental conditions.. The results were, however, not very encouraging since the fruit was also found to be 'exhausted' under the action of the pump and the subsequent admission of air into the desiccator caused a great amount of shrinkage of the fruit. This means that, even if the rot did not grow, the fruit could not be preserved in this way as the fruit would lose its market-value, on account of its shrinkage.

Cellulose, being a carbohydrate of such widespread importance and so abundant in the vegetable kingdom, was given a special trial. The results of the experiments are that at least the vegetative part of the organism does not grow on cellulose. In our experiments three pieces of ordinary filter paper were placed in three Petri dishes and

moistened, sterilized and then cultured and placed under three different conditions : one at the room temperature, another at the temperature of the desiccator under exhaustion and the remaining one at 37° C. None of these indicated any growth. To confirm the results another experiment was arranged in order to see if the rot fungus would properly ferment cellulose. The medium used for this purpose was that of W. B. Sarles, E. B. Fred and W. H. Peterson (Zentralblatt II, 1932, p. 401 Abstrt) to study fermentation by Thermophilic organisms. The experiment however failed to show any cellulose-fermenting power on the part of the fungus, whether at room temperature or at 37° C. The only point discovered was that the organism in the tube developed a special pink colour reaction which could be used as a test. The colour started from the surface of the medium into the empty space of the fermentation tube.

Another thing that was noticed in the experiment with the mango in the desiccator was that the block patch usually associated with the rotting process was not necessarily so conspicuous. Placing inoculated fruits in the desiccator it was found that while the fruit was in the desiccator, no colour changes were apparent although its ulterior examination would reveal a positive invasion of the pulp. The whole surface of the fruit was just as bright and healthy as in any other fresh fruit. It was only when external air was admitted into the desiccator that the fruit suddenly shrank and assumed the characteristic black rotting appearance of spoiled fruits. It seems, therefore, that the colour is only due to an oxidation process probably of a nature similar to those of frequent occurrence in the canning industry.

III.—THE SUMMARY

As the result of the series of experiments carried out in order to investigate the nature of the mango rot and its relation with the problem of the preservation and the export of the mango fruit, we can sum up all our scientific or technical observations as follows :

1. The method of cold storage alone will not work satisfactorily as the activity of the ripening enzymes is not uniform all the time the fruit is in the cold storage.

2. In the majority of cases, it can be demonstrated that the fruit spoilage is due to fungal elements of a definite type and probably of very common occurrence in this part of India. This fungus is seen attacking all kinds of fruits in the market and its action can also be easily observed in the laboratory.

3. This fungoid element works regardless of the variety of mango or, in fact, of the kind of fruit.

4. The potential of the Hydrogen Ion Concentration seems to have no appreciable controlling influence on the microbe, as shown by the fact that only in the case of lemon its attack was delayed to four days while in the case of other fruits it normally occurred on the second day. This delay was probably not due to the pH of the fruit juice alone but to the constituents of the rind also, such as the etherial oils, etc. This fact has been, it will be seen, amply substantiated by the experiments which we have mentioned above. In fact, the rot is capable of growing in all H ion concentrations ranging from 2·2 to 7·4, *i.e.*, verging right on to alkalinity.

5. The microbe under investigation has not the slightest tendency to form spores, and no amount of change in the media, either natural or synthetic, would induce it to take up this protective stage.

6. It follows as a natural sequence of what we have mentioned, that the rot can have only one way of infecting the healthy fruit, *i.e.*, by actual physical contact or through any suitable inoculum. The latter may be the grass or any other similar material used for packing the fruit.

7. Given sufficient moisture, almost any medium will be used as a nutrient substratum by this micro-organism. Saccharides are utilized without exception or preference. Many of the organic acids also serve the purpose well.

8. Certain metals seem to exert a stimulating influence and the acid ion does not seem to make any difference.

9. Phosphoric acid has the same stimulating influence but this has limitations of temperature.

10. Cellulose is not used at all and no growth takes place on a filter paper.

11. As regards the antiseptics (not disinfectants) which could be used in this connexion, some were tried and not one proved to be useful. (See general remarks at the end).

12. Anærobic conditions seem only to paralyse the growth but this effect appears to be attributable more to the desiccation than to the absence of oxygen.

13. Glycerine seems to give the best growth, but all attempts to see whether it is actually produced by the organism as an intermediate breakdown-product from the carbohydrates yielded negative results.

14. In the absence of spores (although we do not exclude the possibility of viable hyphæ) we strongly suspect the insects to be

the carriers. The share that the parent plant may have in handing down the disease to the fruit, remains to be investigated.

IV.—GENERAL REMARKS

In all probability, the only chance of the agriculturist seems to be the complete sterilization of the containers and of all the material used in packing the fruit. In general it may be said that although the fungicides like copper sulphate or potassium permanganate are efficient when used with pure cultures, they are no absolute guarantee against a fresh attack from the surrounding packing material. Surface sterilization of the fruit is not found to be sufficient to prevent rotting, and it is to be noted that rough handling will surely bring about conditions which will render all the surface treatment useless in a fruit of the type of the mango, unless the surrounding material has been properly sterilized. Formalin treatment cannot be recommended ; it is expensive and its effect is not so lasting as that of copper sulphate. Mercuric chloride is out of the question since it is a dangerous poison. It has been found by Gusson and Shutt that even in the case of a consistent product like potato 3 lbs. of it treated for three hours with 1/2000 corrosive sublimate solution would take up from the solution as much as ·05 gr. of $HgCl_2$ which is six times the maximum dose allowable in medicine ; fruit so treated would be inedible.

A SHORT NOTE ON THE DISTRIBUTION OF DIFFERENT TYPES OF LINGULA SPECIES ALONG THE WEST COAST OF THE PRESIDENCY OF BOMBAY

By

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During the course of our work on the Bionomics of Lingula found along the West Coast, we have come across three types of these animals in different localities, *viz.*, the Beyt near Dwarka, Malwan and Vengurla and lastly Ratnagiri, a place between these two extreme points along the coast.

These three types have been compared with Lingula anatina (Lin). The following table gives the points of difference among the types from each other and also from Lingula anatina (Lin).

Table showing differences among the types under consideration when compared with Lingula anatina.

L. anatina	Ratnagiri type.	Malwan type.	Beyt type.
Colour of the shell green or shades of green up to emerald green.	Yellowish green with emerald green concentric lines.	Darker in colour, slightly brownish with green lines. Green anteriorly and posteriorly.	Coppery red or reddish brown with concentric lines of the same colour or sometimes green.
Shell thin and more or less translucent. Shell broader in the middle, sides nearly straight.	Same as in L. anatina; but shell broader at 1|3rd its distance from the posterior end.	Shell thick; in other respects it is similar to L. anatina and Ratnagiri type.	Shell very thick and massive; in other respects it resembles other types.

L. anatina	Ratnagiri type.	Malwan type.	Beyt type.
Setæ on the inner side of the anterior clusters are the longest. Posterior clusters not so prominent.	The longest setæ are in the middle of the anterior clusters. Posterior clusters prominent.	Similar to the Ratnagiri type. Posterior clusters prominent.	Similar to the Ratnagiri type in both respects.
General pigmentation of the body, muscles & mantle lobes slightly yellowish.	Similar to L. anatina.	Similar to L. anatina.	General pigmentation pink. The colour seen even in preserved specimens.
Pallial lacunae not branched.	Sometimes branched.	Sometimes branched.	Often branched.
Nephridia orange in colour. They are marked with maroon lines.	Nephridia yellowish orange. No maroon lines.	Nephridia orange in colour but get fainter towards the nephridio pore.	Dark orange in colour. No maroon lines.
Nephrostome has branched lacunae in the rim.	No branched lacunae.	No branched lacunae.	No branched lacunae.

From the above table it will be seen that the Malwan and the Ratnagiri types differ slightly from each other, the Malwan type having thicker shells with darker colour and bigger size. In all other respects they resemble each other. Both these types differ from Lingula anatina (Lin.) in the arrangement of the anterior clusters of setæ, the colour pattern on the mantle lobes, the absence of maroon lines on the nephridia and in having branched pallial lacunae. With these difference one can assume that these Malwan and Ratnagiri types form two local varieties of Lingula anatina (Lin.).

With regard to the Beyt type, however, the differences between it and Lingula anatina (Lin.) are marked, having a thick, massive and coppery red shell with the pink coloured body. This type resembles more Lingula murphiana (King) in having the red tinge but it differs from the latter in having the shells (valves), the sides of which do not form the inward curve towards the middle of their length. It is one of the chief specific characters of Lingula murphiana (King). Hence it can be presumed that the Beyt type will form a new species.

A further study is being made on this type and results will be communicated shortly.

Obituary

Rev. Father Ethelbert Blatter, S.J.

By the death of the Rev. Ethelbert Blatter, S.J., on the 26th of May, 1934, Botanical Science has lost one of the most outstanding workers in the Systematic Botany of India.

Ethelbert Blatter was born in Switzerland on the 15th of December, 1877. After receiving his elementary education in the village school at Rebstein he went to the College of Sarnen and then to the College of Schwyz. He joined the Society of Jesus in 1896 and came out to India as Professor of Biology, St. Xavier's College, Bombay in 1903. He contributed several articles of scientific importance and before he returned to Europe in 1909 to complete his ecclesiastical studies he had commenced publishing in the pages of the Bombay Natural History Society a series of articles on the Palms of British India and Ceylon which were subsequently published in book form

During his stay in Europe he compiled the Flora of Aden and his Flora Arabica. He returned to India in 1915 as Professor of Botany, St. Xavier's College, and set about immediately building up his extensive collections. Thanks to his assiduous labours, the College to-day possesses one of the finest herbaria in India, (second only in size to that of the Calcutta Botanical Gardens) in which are represented plants from almost the whole of India and the neighbouring Asiatic countries.

By these extensive collections as well as by his numerous writings on Botanical subjects he has made considerable additions to the store of human knowledge, and especially to the botanical literature of the country. He was essentially a Systematic Botanist and devoted the greater part of his attention to the development of the Indian Flora. Though a specialist, he never deprecated the study of other branches of Botany. Since he did not find the time to turn his attention to these himself he was ever ready to encourage even to goad on others to other botanical fields, which have as yet not been cultivated or only to a small extent, fields which he believed afforded plenty of scope for work of greater interest and of greater importance than that in which the systematist is engaged.

Father Blatter has made extensive contributions to Indian Flora and more especially to the Flora of the Bombay Presidency. In 1907

Rev. FATHER ETHELBERT BLATTER, S. J.

during his first visit to India writing on the state of Botany in the Presidency he said "We are going to see soon the completion of Cooke's volumes, a long desired and comprehensive guide to the Flora of the Presidency." Cooke's "Flora of the Bombay Presidency" was completed in 1908. Already in 1917 Father Blatter found that there was much room for additions, alterations, and improvement in these volumes in the light of the more critical treatment of the subject in recent years. Therefore in 1926 after he had been relieved of his arduous duties as Principal and Rector of St. Xavier's College (which posts he held from 1919 to 1924), he set forth to revise the Flora of Bombay. This great work has reached the 23rd part and it is hoped that there will be a number of posthumous additions.

In the matter of his publications though most of them were necessarily highly technical he tried in some instances to cater to the requirements of amateurs by producing literature which could be used by the amateur without losing its truly scientific value. His "Beautiful Flowers of Kashmir" belongs to this category.

It is not possible within the brief space of this article to give a full list of Father Blatter's works. Amongst his outstanding publications are :—The Flora of Aden, The Palms of British India and Ceylon, Revision of the Flora of the Bombay Presidency, Flora Arabica, and the Ferns of Bombay.

Father Blatter's name ranks high amongst those pioneers like J. D. Hooker, Robert Wight, William Roxburgh, Theodore Cooke and others who have by their labours substantially influenced the development of a Scientific Flora of India. He has acquired an international reputation as a botanist and in recognition of his conspicuous important contributions to the knowledge of Asiatic Botany was awarded the Johannes Bruehl Memorial Medal in 1931.

Though Father Blatter had devoted himself to and made his mark in Botany he was a man of varied interests and a versatile genius. He had acquired a sound knowledge of Zoology and Geology. He had a gift for languages, for poetry and art. He possessed a beautiful voice and a feeling for music. In short, he was an all round man.

He was a prominent member of the Bombay University Senate and a Syndic. He was also a member, and for several years a Vice-President of the Bombay Natural History Society, a member of the Indian Botanical Society and a Fellow of the Linnaean Society, and of a number of other Scientific Societies. He was President of the Botany Section of the Indian Science Congress in 1926. He was a

prominent figure in social and scientific circles and on account of his literary and scientific attainments he was held in high esteem by the Bombay Government who considered him to be indispensable for the organisation of the present scheme of the Bombay University Reforms.

His affable manners, his sympathetic disposition and his readiness to help everybody who came to him for succour won for him the affection and regard of his colleagues and assistants, of his large circle of friends and admirers, and of the students both of the College and the Presidency at large in whose memory he will be for ever enshrined as a great benefactor.

J. F. R. d'A.

LIST OF THESES WHICH HAVE BEEN ACCEPTED IN LIEU OF THE EXAMINATION FOR THE M. SC. DEGREE IN BIOLOGICAL SCIENCES DURING 1934-35.

Subject :	Title of thesis.	Name of the candidate.	Teacher.	Place of research.	Remarks.
Botany.	*The study of some Physiological aspects of the Vegetative and Reproductive phases of some Tropical Trees.*	Mr. M. R. Raut.	Prof. R. H. Dastur.	Royal Institute of Science, Bombay.	In course of publication in the "Jour. Ind. Bot. Soc."
Do.	*Marsilia from Poona.*	Mr. G. G. Kolhatkar.	Prof. D. L. Dixit.	Fergusson College. Poona.	....
Do.	*The Physiology of Indian Nodule Bacteria.*	Mr. Abdul Bari.	The Rev. G. Palacios, S. J.	St. Xavier's College, Bombay.	....
Do.	*The effect of Lights on Spectral Intensities on the synthesis of proteins in leaves.*	Mr. U. K. Kanitkar.	Prof. R. H. Dastur.	Royal Institute of Science, Bombay.	In two parts— (*i*) "Michrochemical Tests for proteins in plant cells." Current Science, March, 1935. (*ii*) "The formation of proteins and other nitrogenous substances in light from different sources." in course of publication in the Annals of Botany.
Do.	*Nitrogen contents of the Rice plant (Oryza sativa, L) under different treatments.*	Mr. S. J. Contractor.	Prof. R. H. Dastur.	Do.	In course of publication in Ind. Jour. of Agri.

Subject :	Title of thesis.	Name of the candidate.	Teacher.	Place of research.	Remarks.
Zoology.	*Coccidia from Fish and Lizards.*	Miss R. H. Bana.	Dr. S. B. Setna.	Royal Institute of Science, Bombay.	In course of publication in two parts in the Quarterly Journal of Microscopical Science, London.
Do.	*A contribution to the study of the Bombay Macroplankton with detailed notes on Hydromedusæ Sagittæ and Stomatopod larvæ.*	Miss Piroja B. Gae.	Dr. S. H. Lele.	Do.	A part published in the Bombay Univ. Journal, Vol. III, Pt. 5, as "Some Hydromedusæ of the Bombay Harbour."
Do.	*Bionomics, Anatomy and Morphology of Lingula.*	Mr. G. R. Kshirsagar.	Prof. P. R. Awati.	Do.	A Short note published in ditto.
Botany.	*A study of some aspects of the Physiology of Leaf-movements in Plants.*	Mr. D. E. Wadia.	Prof. R. H. Dastur.	Do.	In course of publication in Annals of Botany.
Zoology.	*Bionomics of Dendrosioma signifer (Selenka) with its Morphology.*	Mr. L. B. Pradhan.	Prof. P. R. Awati.	Do.	Part I published in the Bombay University Journal, Vol. III, Pt. 5.
		For the M.D. Examination.			
	The Rabbit Test for the Diagnosis of Pregnancy.	Mr. S. B. Anklesaria.	....	Motlibai and Petit Hospitals.	Part I published in the Bombay University Journal, Vol. I, Pt. 5.

Reviews

Disease of Children. (Third Edition). Edited by THURSHFELD and PATERSON.

The fact, that the third edition has been published within a few years of the publication of the second edition, speaks for the popularity of this book as well as the anxiety of the Editors to keep abreast with the times. One misses the continuity of thought and uniformity of ideas in publications where different chapters are written by various contributors. But when our conceptions of the diseases are rapidly changing and advances are being made in our knowledge of the various branches of medicine—sometimes with almost kaleidoscopic rapidity, it is impossible for one author to keep pace in all the subjects and hence it is inevitable that different chapters must be contributed by different authorities on the subjects, if the book has to be up-to-date and exhaustive in all the branches. Though Sir Archibald Garrod has ceased to be the Editor, it is fortunate that he still continues to contribute the chapter on the inborn errors of Metabolism—a subject on which he is so well-known an authority. Many new and useful chapters are added to this Edition and they deal with the subject in good details. It would have enhanced the value of the book, if treatments of diseases like Tuberculosis, Leukæmias, etc., had been discussed and dealt with in more exhaustive manner. The fine pictures and diagrams are in entire consonance with the clear printing and attractive get up of the book, which is a valuable addition to the literature in children's diseases.

B. G. V.

Marriage Hygiene. (Vol. I, No. 2).

Contributions in the journal are full of ideas—some controversial and a few revolutionary. The merit of these articles is that they have been written by persons who have frankly expressed their views on subjects in which they have interested themselves. The names on the Editorial Advisory Board would entitle the public to

expect a high standard for this quarterly publication and we wish it can achieve its aim expressed in the opening sentence of rescuing tottering homes.

B. G. V.

Everyday Botany. By L. J. F. Brimble, Macmillan & Co. 1934. pp. 589.

The author, by writing this book, has brought the text-books on Botany in a line with those on other sciences like Physics and Chemistry. As he points out in the preface " the immediate aim has been to present Botany as a progressive branch of science, with the ultimate aim of showing its utilitarian value."

The physiological aspect of plant life is emphasised and the reader is introduced to Ecology and Genetics. Clear diagrams, photographs of plants, places and the scientists are given throughout the book.

The book reveals to the student of Botany the application of this science in every-day life, along with the necessary information of pure academic interest. Information of such varied subjects as fuel, cork, food stuffs, straw, alcohol, plant diseases, soaps and drugs, special uses of plants to men, fruit cultivation and agricultural research, is given in a lucid language.

The directions for the practical work and the exercises increase the value of the book as a student's book. Still, the Indian student would have been much more profited if the book had contained some information about the plants and their surroundings as found in India, and some idea about the Indian research workers and their work.

The book will be very useful in creating interest about scientific knowledge, especially about Botany in the minds of the general public, and will be useful to the students of Medicine, and Agriculture, for the proper understanding of the subject.

S. B. Ranade.

Simple Science. By E. N. da C. Andrade, D.Sc., Ph. D., and Julian Huxley, M.A. (Basil Blackwell Oxford, 676 pages, 8*s*. 6*d*.).

It is interesting to notice that the writers have very satisfactorily achieved their aim in writing this book. Their aim was to present science not as a " school subject ", but as a living body of knowledge which is interwoven into everything around us, whether machines or manufactured articles or the play of natural forces, whether the life of the fields or the mysteries of the laboratory.

The book deals with a number of most absorbing topics, in extremely simple fashion and without even suggesting to the reader, raw or expert, that he is studying science in the stereo-typed divisions known as Physics, Astronomy, Chemistry, Botany, etc.

Science teachers would profit by going through this book very carefully, not so much with a view to learn anything which they probably did not know already, but with the sole desire of trying to follow and appreciate the masterly and lucid manner of exposition employed throughout the pages of this scientific novel. Some of the illustrations are also remarkable in this respect. They are simple and yet fully explanatory.

If matriculation science could be taught in a lively style and as a living subject, science would surely cease to be described as an uninteresting burden. The success of matriculation science depends very largely on the teachers and to those teachers who wish to develop the skill of teaching science, this remarkable book can be very strongly recommended.

G. R. P.

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